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CONTENTS

VIBRATIONS ON POWER LINES IN A STEADY WIND

VI. FORCED VIBRATIONS OF UNIFORM STRINGS AND OF STRINGS WITH STRENGTHENED ENDS UNDER THE ACTION OF UNIFORM PERIODIC FORCES[1]

By R. RUEDY[2]

Abstract

A study of the complete equation expressing the action of a driving force, periodic in time but constant throughout the length of the string and opposed by a damping force proportional to the velocity, leads to formulae suitable for the practical calculation of the shape of standing waves that are produced by a plane wave of sound or by a steady wind. At resonance the amplitude at the midpoint of a uniform string set into a plane wave of sound is proportional to the diameter, to the square root of the intensity of the wave (G erg per sq. cm. per sec.), and inversely proportional to the order of the overtone and to the square root of the frequency. Damping causes the lag between force and motion to differ from point to point, particularly near the nodes, so that even at resonance the wave pattern is not rigorously stationary. On the average, the lag increases from the value zero, obtained when the ratio ν/ν_0 between applied frequency and fundamental frequency is zero, to $\pm\pi/2$ when $\nu/\nu_0 = 1$, increases again from $-\pi/2$ through 0 at $\nu/\nu_0 = 2$, to $\pi/2$ at $\nu/\nu_0 = 3$, and so on.

Action of a Constant Periodic Force upon a Damped String of Uniform Cross Section

When a string that has a cross section of radius a is placed in the field of a plane sound wave of frequency ν and intensity G erg per sec. per sq. cm., the air vibrating in a direction normal to the long axis of the string, each unit length of the string is subject to a lateral force

$$Y = 0.0074\nu a^2\sqrt{G}\epsilon^{-2\pi i\nu t}.$$

The intensity G is equal to the product ps of the sound pressure p and the velocity s of the vibrating air, where p and s denote root mean square values. In ordinary conversation the intensities are of the order of the erg at a distance of a few feet from the source; this intensity corresponds to a pressure variation of 1 dyne per cm., or one-millionth of atmospheric pressure. A sound intensity corresponding to a pressure amplitude of 1 dyne per sq. cm. at a frequency of 1,000 cycles per sec. is sometimes used as a reference point in the measurement of loudness. The pressure variations that occur in speech or music are below 1/100 atm. at the ear.

Somewhat stronger lateral forces are exerted upon a string when a steady wind of velocity U cm. per sec. blows at a right angle against the wire, and the amplitudes obtained in winds with a speed of 500 to 1200 cm. per sec., a range most favourable to the production of vibrations, become visible to the unaided eye.   As shown by theory and confirmed by experiments, the amplitude of the alternating force acting in a direction at right angles to both the uniform wind and the string, as though it were produced by an electrodynamic effect, is equal to

$$G = 1.46\rho a \frac{U^2}{2},$$

where ρ is the density of the air (1.25×10^{-3} at $10°$ C.) and U does not normally exceed 12 metres per sec. for winds that can be called steady.   Since the frequency of vibration is $\nu = \dfrac{U}{10a}$,

$$G = 0.09a^3\nu^2;$$

the alternating force exerted upon a wire by a steady wind increases, therefore, more rapidly with the radius of the wire and the frequency of the sound than do the forces obtained in the field of a plane wave.

The equation of motion of a string of mass ρ_0 per unit length set into vibration by a force $Fe^{-2\pi i\nu t}$ dyne per cm. that is periodic in time but at any moment constant throughout the length $l = 2L$ of the string, and opposed by a frictional force proportional to the velocity but independent of the actual frequency, $R(x)\,\partial y/\partial t$ dyne per unit length, is

$$\frac{\partial^2 y}{\partial t^2} = \frac{S}{\rho_0}\frac{\partial^2 y}{\partial x^2} + \frac{F}{\rho_0}\epsilon^{-2\pi i\nu t} - \frac{R}{m}\frac{\partial y}{\partial t}.$$

On the assumption that F and R are constant, a solution exists in the form

$$y = Y(x)T(t) = Y(x)\epsilon^{-2\pi i\nu t},$$

so that

$$\frac{d^2 Y}{dx^2} + \frac{4\pi^2\nu^2 + 4\pi i\nu k}{c^2}\,Y + f = \frac{d^2 Y}{dx^2} + \frac{w^2}{c^2}\,Y + f = 0,$$

where

$$f = F/S \text{ and } 2k = R/m.$$

In accordance with the theory of linear differential equations, the solution consists of the complementary function $A\cos wx/c$ obtained when F is zero, and a particular integral.   A particular integral of the present equation is found by assuming Y to be a constant, namely, according to the equation, equal to $-fc^2/w^2$, with

$$w^2 = 4\pi^2\nu^2 + 4\pi i\nu k = 4\pi^2\nu^2\left(1 + \frac{ik}{\pi\nu}\right),$$

and for the small values of $2k = R/m$ normally encountered there follows

$$w = 2\pi\nu\left(1 + \frac{ik}{2\pi\nu}\right) = \omega + ik.$$

A complete solution satisfying the boundary conditions $Y = 0$ at $x = -L$ and at $x = +L = l/2$ is

$$Y(x) = \frac{F}{\rho_0 w^2} \frac{\cos\dfrac{w}{c}x - \cos\dfrac{wl}{2c}}{\cos\dfrac{wl}{2c}},$$

so that

$$Y(x) = \frac{F}{4\pi^2\rho_0\nu^2\left(1 + \dfrac{ik}{\nu\pi}\right)} \left[\frac{\cos\left(\dfrac{\nu}{\nu_0}\dfrac{\pi}{2} + \dfrac{ik}{4\nu_0}\right)\dfrac{x}{L}}{\cos\left(\dfrac{\nu}{\nu_0}\dfrac{\pi}{2} + \dfrac{ik}{4\nu_0}\right)} - 1 \right]$$

for a small value of k. The solution has the form $Y(x) = A \cos (bx + d) - F/b^2S$. A pure harmonic wave shape is not to be expected since the external force is not proportional to the displacement along the freely vibrating stretched wire.

Discussion of the Equation

When $k = 0$, the expression for the amplitude reduces to the formula given in treatises on sound

$$Y(x) = \frac{F}{4\rho_0\pi^2\nu^2} \left[\frac{\cos\dfrac{\nu}{\nu_0}\dfrac{\pi}{2}\dfrac{x}{L}}{\cos\dfrac{\nu}{\nu_0}\dfrac{\pi}{2}} - 1 \right] = \frac{F}{4\pi^2\rho_0\nu^2} \frac{\cos\dfrac{\nu}{\nu_0}\dfrac{\pi}{2}\dfrac{x}{L}}{\cos\dfrac{\nu}{\nu_0}\dfrac{\pi}{2}} - \frac{F}{4\pi^2\rho_0\nu^2};$$

it corresponds to a single yet slightly distorted wave that instead of having its equilibrium position along $Y = 0$ is symmetrical, at a given frequency, with respect to the straight line $Y = -F/4\rho_0\pi^2\nu^2$. The excursions in the negative direction are therefore deeper than the displacements in the positive direction. The amplitude at the centre reduces to zero when ν/ν_0 is a multiple of four. The amplitudes tend to become infinite throughout the length of the string whenever the applied frequency is an odd multiple of the fundamental frequency ν_0. Since, according to the Fourier development,

$$1 = \frac{4}{\pi}\left(\sin \pi \frac{x}{l} + \frac{1}{3}\sin 3\pi \frac{x}{l} + \frac{1}{5}\sin 5\pi \frac{x}{l} + \cdots\right)$$

for any value of x between 0 and l, a constant force F has no components that correspond to an even number of loops, and none of the even multiples of the fundamental frequency can be expected to produce resonance.

In order to arrive at results that apply to actual measurements it is necessary to include the damping force, at least at or near the resonance frequencies,

where ν/ν_0 is an odd multiple of $\pi/2$, so that

$$Y(x) = \frac{\left(1 - \dfrac{ik}{\nu\pi}\right)F}{4\rho_0\pi^2\nu^2\left(1 + \dfrac{k^2}{\pi^2\nu^2}\right)}\left[\frac{\sin\dfrac{\nu}{\nu_0}\dfrac{\pi}{2}\dfrac{x}{L}\sinh\dfrac{k}{4\nu_0}\dfrac{x}{L} + i\cos\dfrac{\nu}{\nu_0}\dfrac{\pi}{2}\dfrac{x}{L}\cosh\dfrac{k}{4\nu_0}\dfrac{x}{L}}{\pm\,\sinh\dfrac{k}{4\nu_0}} - 1\right],$$

where the plus sign applies to multiples of $\pi/2$, $5\pi/2$, $9\pi/2$, etc., and the minus sign to $3\pi/2$, $7\pi/2$, $11\pi/2$, etc. Providing that, as usually obtains, $k/4\nu_0 < 0.03$, and therefore $(1 + ik/2\pi\nu)^2$ is closely equal to $\left(1 + \dfrac{ik}{\nu\pi}\right)$, the amplitude is

$$Y(x) = \frac{F}{\pm\,4\rho_0\pi^2\nu_0^2\,\dfrac{\nu^2}{\nu_0^2}}\,\frac{\cos\dfrac{\nu}{\nu_0}\dfrac{\pi}{2}\dfrac{x}{L}}{\dfrac{k}{4\nu_0}}\,\epsilon^{i(\phi+\phi_1)}\quad\text{(at resonance)}$$

$$\tan\phi = -\frac{k}{\pi\nu}$$

$$\tan\phi_1 = \frac{1}{\dfrac{k}{4\nu_0}\dfrac{x}{L}\tan\dfrac{\pi}{2}\dfrac{x}{L}}.$$

For arbitrary values of ν the expression containing the trigonometric functions in the formula for the wave shape may be written in the form

$$\frac{r_1}{r_2}\,\epsilon^{i(\phi_1-\phi_2)} = \frac{\cos\left(\dfrac{\nu}{\nu_0}\dfrac{\pi}{2} + i\dfrac{k}{4\nu_0}\right)\dfrac{x}{L} - \cos\left(\dfrac{\nu}{\nu_0}\dfrac{\pi}{2} + i\dfrac{k}{4\nu_0}\right)}{\cos\left(\dfrac{\nu}{\nu_0}\dfrac{\pi}{2} + i\dfrac{k}{4\nu_0}\right)}$$

where

$$r_1^2 = \cos^2\frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L} + \cos^2\frac{\nu}{\nu_0}\frac{\pi}{2} + \sinh^2\frac{k}{4\nu_0}\frac{x}{L} + \sinh^2\frac{k}{4\nu_0}$$

$$- 2\cos\frac{\nu}{\nu_0}\frac{\pi}{2}\cos\frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}\cosh\frac{k}{4\nu_0}\cosh\frac{k}{4\nu_0}\frac{x}{L}$$

$$- 2\sin\frac{\nu}{\nu_0}\frac{\pi}{2}\sin\frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}\sinh\frac{k}{4\nu_0}\sinh\frac{k}{4\nu_0}\frac{x}{L}$$

$$= \sin^2\frac{\nu}{\nu_0}\frac{\pi}{4}\left(\frac{x}{L} + 1\right)\sin^2\frac{\nu}{\nu_0}\frac{\pi}{4}\left(\frac{x}{L} - 1\right)$$

$$+ \sin^2\frac{\nu}{\nu_0}\frac{\pi}{4}\left(\frac{x}{L} + 1\right)\sinh^2\frac{k}{8\nu_0}\left(\frac{x}{L} - 1\right)$$

$$+ \sin^2\frac{\nu}{\nu_0}\frac{\pi}{4}\left(\frac{x}{L} - 1\right)\sinh^2\frac{k}{8\nu_0}\left(\frac{x}{L} + 1\right)$$

$$+ \sinh^2\frac{k}{8\nu_0}\left(\frac{x}{L} + 1\right)\sinh^2\frac{k}{8\nu_0}\left(\frac{x}{L} - 1\right)$$

$$r_2{}^2 = \cos^2 \frac{\nu}{\nu_0} \frac{\pi}{2} \cosh^2 \frac{k}{4\nu_0} + \sin^2 \frac{\nu}{\nu_0} \frac{\pi}{2} \frac{x}{L} \sinh^2 \frac{k}{4\nu_0} \frac{x}{L}$$

$$= \cos^2 \frac{\nu}{\nu_0} \frac{\pi}{2} + \sinh^2 \frac{k}{4\nu_0},$$

with slight simplifications when ν/ν_0 is an even or an odd number. Moreover

$$\tan \phi_1 = - \frac{\sin \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \sinh \dfrac{k}{4\nu_0} - \sin \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \dfrac{x}{L} \sinh \dfrac{k}{4\nu_0} \dfrac{x}{L}}{\cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \cosh \dfrac{k}{4\nu_0} - \cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \dfrac{x}{L} \cosh \dfrac{k}{4\nu_0} \dfrac{x}{L}}$$

$$\tan \phi_2 = - \tan \frac{\nu}{\nu_0} \frac{\pi}{2} \tanh \frac{k}{4\nu_0}.$$

In particular, when $\dfrac{\nu}{\nu_0} = 1, 3, 5 \ldots$

$$\tan \phi_1 = - \tan \frac{\nu}{\nu_0} \frac{\pi}{2} \frac{x}{L} \tanh \frac{k}{4\nu_0} \frac{x}{L} \mp \frac{\sinh \dfrac{k}{4\nu_0}}{\cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \dfrac{x}{L} \cosh \dfrac{k}{4\nu_0} \dfrac{x}{L}},$$

and when $\dfrac{\nu}{\nu_0} = 2, 4 \ldots$

$$\tan \phi_2 = \frac{\sin \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \dfrac{x}{L} \sinh \dfrac{k}{4\nu_0} \dfrac{x}{L}}{\pm \cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \cosh \dfrac{k}{4\nu_0} - \cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \dfrac{x}{L} \cosh \dfrac{k}{4\nu_0} \dfrac{x}{L}}.$$

$$\tan \phi_2 = \mp \infty \quad \text{or } \phi_2 = \pm \frac{\pi}{2} \quad \text{when } \frac{\nu}{\nu_0} \doteq 1, 3, 5 \ldots$$

$$\tan \phi_2 = 0 \qquad \text{or } \phi_2 = 0 \qquad \text{when } \frac{\nu}{\nu_0} \doteq 2, 4 \ldots$$

$$\tan (\phi_1 - \phi_2) = 1/\tan \phi_1 \quad \text{for } \frac{\nu}{\nu_0} \doteq 1, 3, 5 \ldots$$

$$\tan (\phi_1 - \phi_2) = \tan \phi_1 \qquad \text{for } \frac{\nu}{\nu_0} \doteq 2, 4 \ldots$$

When, as is usually the case, k is smaller than 0.1 the development in series of the sinh and cosh functions may be confined to the first terms; there follows $\left(\text{except when } x/L = 0 \text{ and } \cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} = 0\right)$,

$$\frac{r_1}{r_2} = \left(\frac{\cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \dfrac{x}{L}}{\cos \dfrac{\nu}{\nu_0} \dfrac{\pi}{2}} - 1 \right) \frac{1}{\sqrt{\cosh^2 \dfrac{k}{4\nu_0} + \tan^2 \dfrac{\nu}{\nu_0} \dfrac{\pi}{2} \dfrac{x}{L} \sinh^2 \dfrac{k}{4\nu_0} \dfrac{x}{L}}}$$

$$\tan \phi_1 = -\frac{k}{4\nu_0} \frac{\sin \frac{\nu}{\nu_0}\frac{\pi}{2} - \frac{x}{L}\sin \frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}}{\cos \frac{\nu}{\nu_0}\frac{\pi}{2} - \cos \frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}}$$

$$\tan \phi_2 = -\frac{k}{4\nu_0} \tan \frac{\nu}{\nu_0}\frac{\pi}{2}$$

or, finally, with $\tan \phi = \frac{k}{\nu\pi}$, a small quantity,

$$Y(x) = \frac{F}{4\rho_0\pi^2\nu_0^2\nu^2/\nu_0^2}\frac{r_1}{r_2}\epsilon^{i(\phi+\phi_1-\phi_2)}\left(\frac{\cos \frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}}{\cos \frac{\nu}{\nu_0}\frac{\pi}{2}} - 1\right)$$

for the amplitudes off resonance. The frequency appears in the formula in the ratio ν/ν_0, so that the same solution holds for all strings, regardless of their fundamental frequency. As to the phase difference,

$$\tan (\phi + \phi_1 - \phi_2) \doteq \tan \phi + \tan (\phi_1 - \phi_2)$$

or

$$\tan (\phi + \phi_1 - \phi_2) \doteq -\frac{k}{4\nu_0}\left(\frac{2}{\frac{\nu}{\nu_0}\frac{\pi}{2}} + \frac{\sin \frac{\nu}{\nu_0}\frac{\pi}{2} - \frac{x}{L}\sin \frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}}{\cos \frac{\nu}{\nu_0}\frac{\pi}{2} - \cos \frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}} - \tan \frac{\nu}{\nu_0}\frac{\pi}{2}\right)$$

(off resonance).

In other words, the amplitudes produced off resonance by a uniform alternating force along a uniform string with viscous damping are equal to the amplitudes of the undamped string multiplied by a correction factor that is virtually equal to unity, and a lag factor that varies from point to point. Owing to the factor $k/4\nu_0$, the lag or phase difference is small, with two exceptions. Large phase angles are obtained along the entire string in the neighbourhood of the resonance frequencies $\nu/\nu_0 = 1$, $\nu/\nu_0 = 3$, etc., where $\tan \frac{\nu}{\nu_0}\frac{\pi}{2}$ increases without limit. The average lag increases from the value zero, obtained when the ratio ν/ν_0 is nearly equal to zero, to $\pm\pi/2$ when ν/ν_0 is about unity, increases again from $-\pi/2$ to zero at $\nu/\nu_0 = 2$, and to $\pi/2$ at $\nu/\nu_0 = 3$; then the same changes are repeated. The phase angle is also large, regardless of the frequency, at those points of the string for which

$$\cos \frac{\nu}{\nu_0}\frac{\pi}{2} = \cos \frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}.$$

Several series of solutions exist for this equation. By virtue of the relation $\cos a = \cos (2\pi - a) = \cos (4\pi - a)$, etc. where a stands for $\nu/\nu_0 \times \pi/2$,

the equation is satisfied by values of x/L such that, for instance,

$$2\pi - \frac{\nu}{\nu_0}\frac{\pi}{2} = \frac{\nu}{\nu_0}\frac{\pi}{2}\frac{x}{L}$$

FIG. 1. *Shapes of standing waves of a damped string stretched between rigid supports when driven by a uniform force $F/4\rho_0\pi^2\nu_0^2$ of frequency ν. The fundamental frequency of the string is ν_0. Phase differences along the string are neglected. The amplitudes at resonance are inversely proportional to $k/4\nu_0$, and the curves shown for $\nu/\nu_0 = 1$, $\nu/\nu_0 = 3$, $\nu/\nu_0 = 5$, correspond to the large and constant value $k/4\nu_0 = 0.1$. Points at which the phase difference attains large values and changes rapidly are marked by circles.*

or

$$4 - \frac{\nu}{\nu_0} = \frac{\nu}{\nu_0}\frac{x}{L},$$

providing that a positive fraction less than unity is obtained for x/L; in other words, ν/ν_0 must exceed 2 and be less than 4. Another group of points is deduced from the relation $\cos a = \cos (2\pi + a)$ or

$$\frac{\nu}{\nu_0} - 4 = \frac{\nu}{\nu_0}\frac{x}{L}.$$

With this choice the solutions x/L lie near the nodes of the string, and since the phase difference varies rapidly in their neighbourhood, the wave pattern fails to become completely stationary, a conclusion that is in agreement with careful measurements of the amplitudes of ordinary strings as well as of power lines.
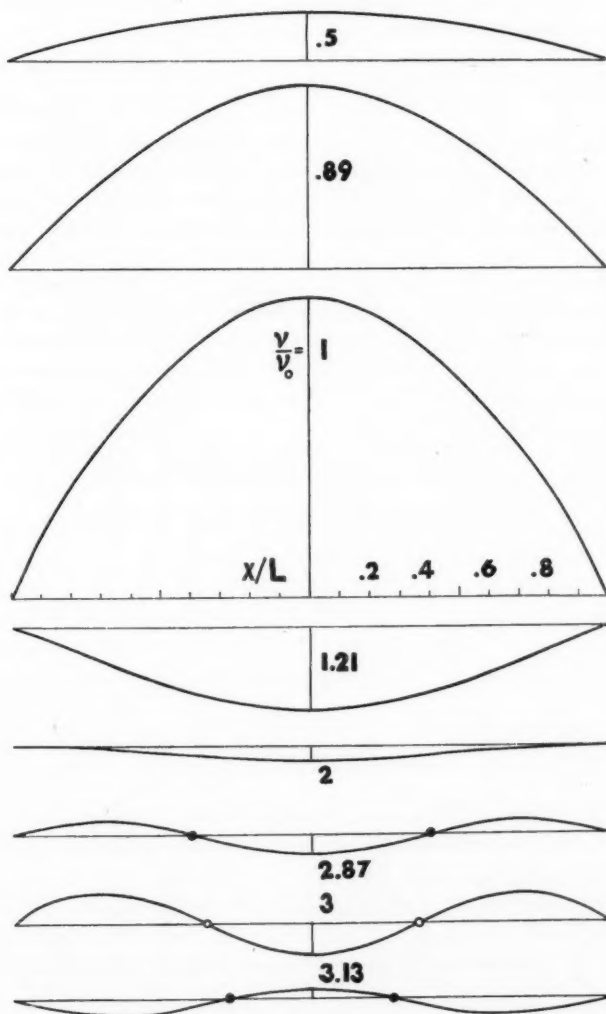
Fig. 1 shows the shapes of steady state motion of a damped string stretched between rigid supports and driven by a uniform force $F/4\rho_0\pi^2\nu_0^2$, of frequency ν. The fundamental frequency of the string is ν_0. Phase differences are disregarded, but the points at which rapid increases and decreases in phase angle occur are marked by circles. The amplitudes at resonance are computed on the assumption that $k/4\nu_0 = 0.1$; normally, this fraction is much smaller. Fig. 2 represents the tan of the angle by which the motion lags behind the force for various ratios ν/ν_0, the fraction $k/4\nu_0$ being equal to unity. The tan of the phase angle is proportional to $k/4\nu_0$.
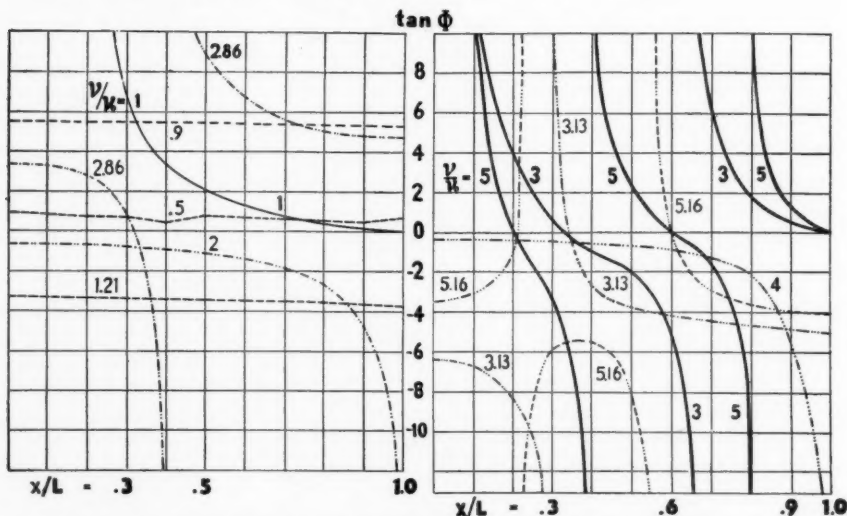

FIG. 2.   The tan of the total phase angle ($\phi_1 + \phi_1 - \phi_2$) in the steady motion of a damped string with fixed ends.   For the frequencies off resonance the tan is proportional to $k/4\nu_0$; for the resonance frequency the tan is about inversely proportional to $k/4\nu_0$ and quite large.

The curves are based on the assumption that $\frac{k}{4\nu_0} = 1$.

Practical Applications

For viscous motion of the air the damping coefficient of a string of diameter $d = 2a$ is given by a formula derived by Stokes

$$k = \frac{4 \sqrt{\pi \rho \eta \nu}}{\rho_0 d} ,$$

where η is the viscosity of the air (1.77×10^{-5} at $10°$ C.), ρ its density (1.25×10^{-3} at $10°$ C.), and ρ_0 the density of the material from which the string is made. For quiet air at about $10°$ C.

$$k = \frac{0.0033 \sqrt{\nu}}{\rho_0 d} .$$

It may be considered as approximately independent of the frequency, particularly at high frequencies. With this coefficient the formula for the greatest amplitude at the midpoint becomes

$$Y(0)_r \doteq \frac{\nu_0 F}{\pi^2 \rho_0 \nu^2 k} \doteq \frac{300 \nu_0 F d}{\pi^2 \nu^{5/2}} .$$

When F is the force acting in a plane wave of sound at right angles to the string

$$Y(0)_r \doteq \frac{0.0723d \sqrt{G}}{\nu^{1/2}} \frac{\nu_0}{\nu} \text{ cm} \doteq \frac{d \sqrt{G}}{14 \nu^{1/2}} \frac{\nu_0}{\nu} .$$

For sounds of ordinary intensity G and frequency, the motion of a thin string, produced by resonance in the field of a plane sound wave, is too small to be detected even with a microscope. A thin stretched wire might nevertheless be used for exploring the distribution of the intensity in front of a loudspeaker emitting low frequencies in great strength.

When the string is exposed to a steady wind, the amplitude at the midpoint becomes equal to

$$Y(0)_r \doteq 0.9d \frac{\nu_0}{\sqrt{\nu}} \text{ cm.}$$

With wires that are one or several centimetres thick and tuned to frequencies of a few cycles per second, as is the case with power lines, the amplitude at the centre exceeds 1 mm. even if the external force creates a frequency of as many as 50 cycles per sec. Measurements give amplitudes of several millimetres.

The amplitudes of a wire stretched out in a magnetic field and traversed by an alternating current may be obtained in a similar way.

Response of a Strengthened Damped String to a Uniform Alternating Force

When the radius a of the cross section of a string of length $l = 2L$ increases according to the law $a_0(1 \pm \lambda x/L)^{m/2}$, on both sides of a midpoint taken as the origin, the mass per unit length increases as $\rho_0(1 \pm \lambda x/L)^m$, and the force

exerted in a transverse direction upon unit length of a string by a sound field of intensity G ergs per sec. per sq. cm. is

$$F = 0.0074 \nu a^2 (1 \pm \lambda x/L)^m \sqrt{G} \epsilon^{-2\pi i \nu t}$$

Apart from the time function the equation of motion of the string is, with $\eta = y/L$ and $\xi = 1 + x/L$,

$$\frac{d^2\eta}{d\xi^2} + \omega^2 \frac{L^2}{4\lambda^2} \frac{\rho_0}{S} \xi^m = \frac{F}{S} \xi^m.$$

The solution of the equation without second member is known. A particular solution of the complete equation is $F\lambda^2\nu_0^2/\pi^2\nu^2S$, and since

$$\frac{d^2}{d\xi^2}\left(\xi^{1/2} J_{\frac{\pm 1}{m+2}}\left(\frac{2\sqrt{b}}{m+2}\,\xi^{\frac{m+2}{2}}\right)\right) = -\, b\xi^{m+1/2} J_{\frac{\pm 1}{m+2}}\left(\frac{2\sqrt{b}}{m+2}\,\xi^{\frac{m+2}{2}}\right),$$

a complete solution satisfying the boundary conditions that $\eta = y/L$ is equal to zero at the ends, where $\xi = 1 + \lambda$, but not at $\xi = 1$, or at the centre, is

$$\eta = \frac{\lambda^2}{\pi^2}\frac{\nu_0^2}{\nu^2}\frac{F}{S}\left[\frac{\xi^{1/2} J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}\xi^{\frac{m+2}{2}}\right)}{(1+\lambda)^{1/2} J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right)} - 1\right].$$

For the sake of brevity a corresponding term proportional to $\sqrt{\xi}\, J_{1/(m+2)}$ has been omitted from numerator and denominator. In the present example, terms in $J_{+1/(m+2)}$ need not be included because a constant force can be represented as a sum of products of ξ by $J_{-1/(m+2)}$ alone; indeed, since

$$x^\mu = \sum_{r=1}^\infty \frac{2 J_\mu(j_r x)}{j_r J_{\mu+1}(j_r)}\qquad \text{where } J_\mu(j_r) = 0,$$

$$\xi^{-1/2} = \sum_{r=1}^\infty \frac{2 J_{-\frac{1}{m+2}}\left(j_r \xi^{\frac{m+2}{2}}\right)}{j_r J_{\frac{m+1}{m+2}}(j_r)}$$

$$1 = \sum_{r=1}^\infty \frac{2 \xi^{1/2} J_{-\frac{1}{m+2}}\left(j_r \xi^{\frac{m+2}{2}}\right)}{j_r J_{\frac{m+1}{m+2}}(j_r)}$$

$$\xi^m = \sum_{r=1}^\infty \frac{2 \xi^m \xi^{1/2} J_{-\frac{1}{m+2}}\left(j_r \xi^{\frac{m+2}{2}}\right)}{j_r J_{\frac{m+1}{m+2}}(j_r)}$$

The amplitude at the centre reduces to zero at the frequencies for which

$$J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}\right) = (1+\lambda)^{1/2} J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right).$$

Since both $(1 + \lambda)^{1/2}$ and $(1 + \lambda)^{(m+2)/2}$ exceed unity, a series of such solutions exist. When ν is a real quantity the amplitude becomes infinite throughout the length of the string for the ratio

$$\frac{\nu}{\nu_0} = \lambda(m+2)(1+\lambda)^{\frac{2}{m+2}}\frac{j_r}{\pi},$$

where j_r is a root of $J_{-1/(m+2)}$.

In order to take the damping force into account, a very important factor from the practical point of view, a complex value $w = \nu + ik/2\pi$ is put in the place of ν, and since for $m = 2$ the factor $\pi/\lambda(m + 2)$ varies between 0.785, for $Q = 4$, and 0.26, for $Q = 16$, the asymptotic formulae for the Bessel functions are suitable for frequencies above the thirtieth overtone. For other frequencies, advantage is taken of the relation

$$J_\mu(x+iy) = \sum_{s=0}^{\infty} J_{\mu-s}(x)J_s(iy) + \sum_{s=1}^{\infty}(-1)^s J_{\mu+s}(x)J_s(iy)$$

or

$$J_\mu(x+iy) = J_\mu(x)J_0(iy) + J_1(iy)\left(J_{\mu+1}(x) - J_{\mu-1}(x)\right)$$
$$+ J_2(iy)\left(J_{\mu+2}(x) - J_{\mu-2}(x)\right)$$

where, in the present problem,

$$x = \frac{\pi}{\lambda(m+2)}\frac{\nu}{\nu_0}\xi^{\frac{m+2}{2}}$$

$$y = \frac{k}{2\lambda(m+2)\nu_0}\xi^{\frac{m+2}{2}},$$

and k is a small quantity. A solution that is sufficiently accurate for practical purposes is

$$\eta = \frac{\lambda^2}{\pi^2}\frac{\nu_0^2}{w^2}\frac{F}{S}\left(\frac{N}{D}-1\right) = \frac{\lambda^2(1-ik/2\pi)}{\pi^2\nu^2/\nu_0^2}\frac{F}{S}\left(\frac{N}{D}-1\right),$$

where

$$\frac{N}{\xi^{1/2}} = J_{-\frac{1}{m+2}}(x)J_0(y) - 2J_1(y)dJ_{-\frac{1}{m+2}}(x)/dx$$

$$\frac{D}{(1+\lambda)^{1/2}} = J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right)J_0\left(\frac{ik}{2\lambda(m+2)\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right)$$

$$+ \left(J_{\frac{m+1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right)\right.$$

$$\left. - J_{-\frac{m+3}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right)\right)J_1\left(\frac{ik}{2\lambda(m+2)\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right).$$

At resonance the first term of the denominator vanishes with

$$J_{-\frac{1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_c}(1+\lambda)^{\frac{m+2}{2}}\right) = 0,$$

and the second term is small, so that N/D is much larger than unity.   When the square and higher terms of $k/4\lambda\nu_0$ are neglected, there follows

$$\frac{(1+\lambda)^{1/2}N}{\xi^{1/2}D}$$

$$= \frac{J_{\frac{-1}{m+2}}(x) \; - \cdot 2J_1(y)dJ_{\frac{-1}{m+2}}(x)/dx}{\frac{ik(1+\lambda)^{\frac{m+2}{2}}}{4\lambda(m+2)\nu_0}\left(J_{\frac{m+1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right) - J_{-\frac{m+3}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right)\right)},$$

and for the amplitude at the centre

$$\eta_0 =$$

$$\frac{\lambda^2}{\pi^2}\frac{\nu^2}{\nu_0^2}\frac{F}{S}\frac{J_{\frac{-1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}\right)\epsilon^{-i\pi/2}}{\frac{k(1+\lambda)^{\frac{m+3}{2}}}{4\lambda(m+2)\nu_0}\left(J_{\frac{m+1}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right) - J_{-\frac{m+3}{m+2}}\left(\frac{\pi/\lambda}{m+2}\frac{\nu}{\nu_0}(1+\lambda)^{\frac{m+2}{2}}\right)\right)}.$$

The functions $J_{5/4}$ and $J_{-5/4}$ required for dealing with the vibrations when $m = 2$ have been computed for variables up to 8, and are represented in Figs. 3 and 4.   For larger variables the asymptotic expansions are suitable. For other values of m, no tables for the functions in the denominator are
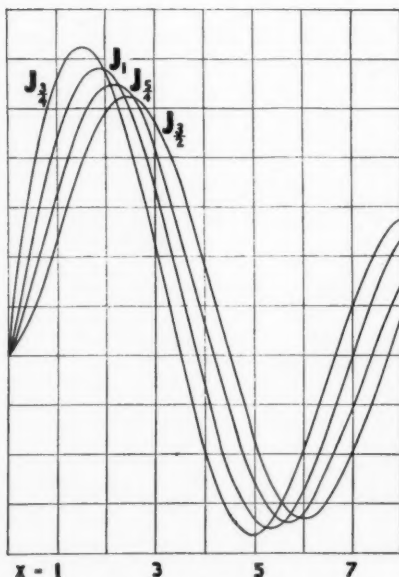

FIG. 3.   The Bessel function $J_{5/4}(x)$, with $J_{3/4}$, $J_{4/4}$, and $J_{9/4}(x)$ for comparison.
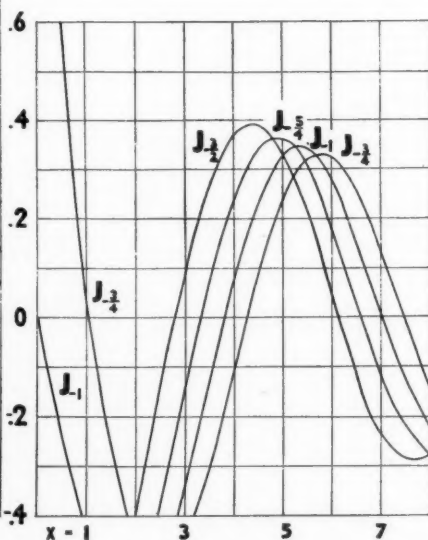
FIG. 4.   The Bessel function $J_{-5/4}(x)$, with $J_{-9/4}$ and $J_{-3/4}$ for comparison.

available, and a comparison with the uniform string can therefore be made only from case to case for a given ν/ν_0 and a given λ.

Response of a Strengthened String to Arbitrary Non-uniform Alternating Forces

When the force acting upon unit length of the string at the point x is $R(\xi)\epsilon^{-2\pi i\nu t}$, the equation of motion of the string

$$\frac{d^2\eta}{d\xi^2} + \frac{\pi^2\nu^2}{\lambda^2\nu_0^2}\,\xi^m\eta = -\frac{LF(\xi)}{S\lambda^2} - i\,\frac{\omega}{\lambda^2}\,\frac{R(\xi)}{S}$$

can be solved either by using Lagrange's method of the variation of the constants of integration, or by means of an analysis into normal modes of motion. Both methods use the solutions obtained when the right-hand side of the equation is zero, with or without regard to the boundary conditions.

In a few cases the solutions are obtained in finite form. Since, for instance,

$$\int z^{\mu+1}J_\mu(z)dz = z^{\mu+1}J_{\mu+1}(z)$$

and

$$\int z^\mu J_{\mu-1}(z)dz = z^\mu J_\mu(z),$$

there follows, with $\mu = \dfrac{1}{m+2}$ and $z = \alpha\xi^{\frac{m+2}{2}}$,

$$\int \xi^{m+1}\sqrt{\xi}J_{\frac{1}{m+2}}\left(\alpha\xi^{\frac{m+2}{2}}\right) = \frac{2}{\alpha\,(m+2)}\,\xi^{\frac{m+3}{m+2}}J_{\frac{m+3}{m+2}}\left(\alpha\xi^{\frac{m+2}{2}}\right)$$

$$\int \xi^{m+1}\sqrt{\xi}J_{-\frac{1}{m+2}}\left(\alpha\xi^{\frac{m+2}{2}}\right) = \frac{-2}{\alpha\,(m+2)}\,\xi^{\frac{m+3}{m+2}}J_{-\frac{m+3}{m+2}}\left(\alpha\xi^{\frac{m+2}{2}}\right)$$

When the external force varies as ξ^{m+1}, the expressions occurring in Lagrange's solutions of the equation of forced motion

$$\eta = c_1\eta_1 + \frac{\pi}{m+2}\,\frac{\eta_1}{\sin\dfrac{\pi}{m+2}}\int \eta_2 R(\xi) + c_2\eta_2 - \frac{\pi}{m+2}\,\frac{\eta_2}{\sin\dfrac{\pi}{m+2}}\int \eta_1 R(\xi)$$

where

$$\eta_1 = \sqrt{\xi}J_{\frac{1}{m+2}}\left(\alpha\xi^{\frac{m+2}{2}}\right)$$

$$\eta_2 = \sqrt{\xi}J_{-\frac{1}{m+2}}\left(\alpha\xi^{\frac{m+2}{2}}\right)$$

are readily integrated. The boundary conditions are introduced and the complete solution follows.
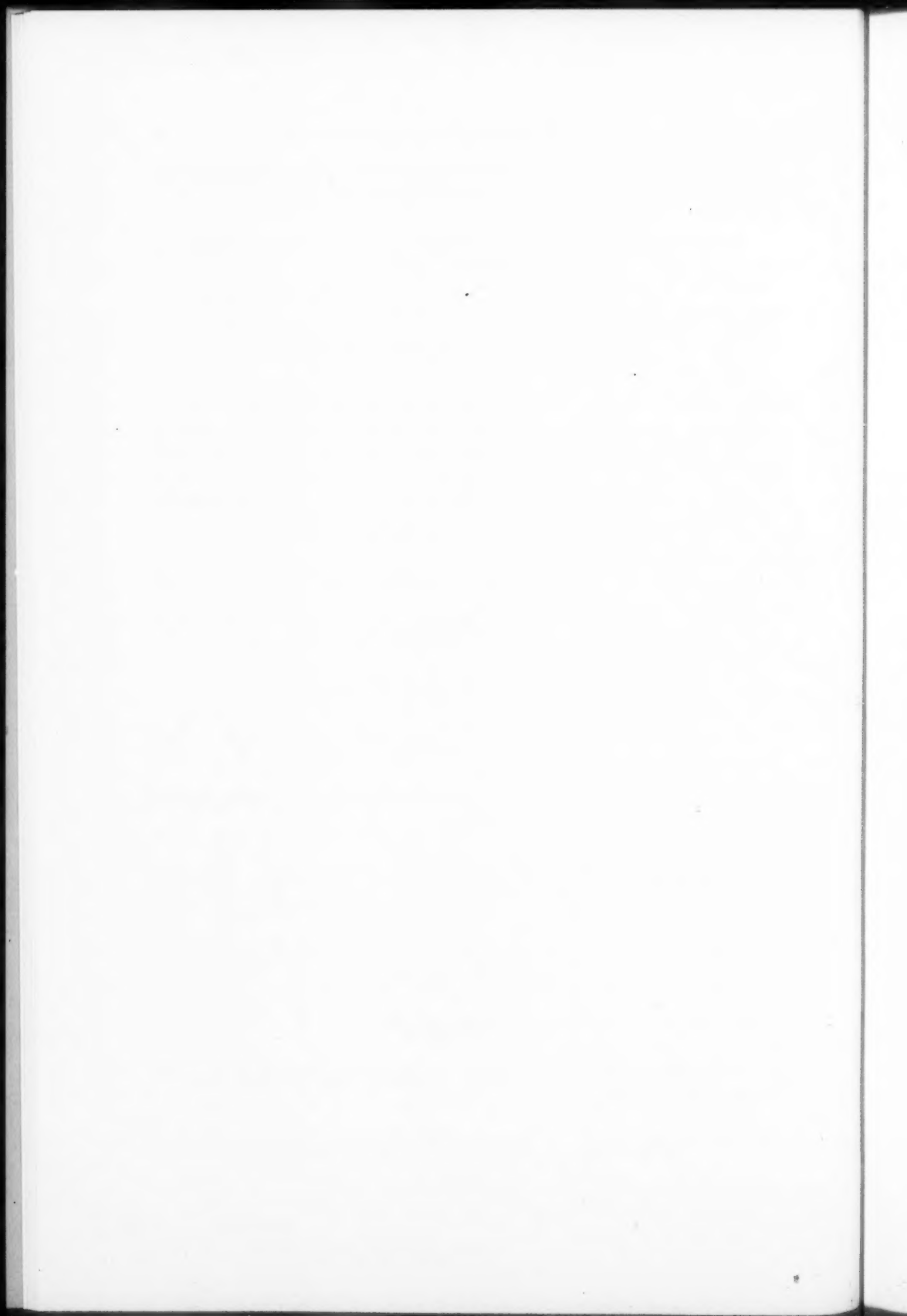
THE ALKALOIDS OF *SENECIO* SPECIES

III. *SENECIO INTEGERRIMUS, S. LONGILOBUS, S. SPARTIOIDES* AND *S. RIDELLII*[1]

BY RICHARD H. F. MANSKE[2]

Abstract

Senecionine is the main alkaloid of *Senecio integerrimus*, but a small amount of a new alkaloid, *integerrimine* ($C_{18}H_{25}O_5N$), was also found. *S. longilobus* contains *longilobine* ($C_{18}H_{23}O_5N$) and *S. ridellii* contains *ridelliine* ($C_{18}H_{23}O_6N$), both alkaloids being new. In addition to the main alkaloid of *S. spartioides*, which was identified as seneciphylline, a minor base, *spartioidine* ($C_{18}H_{23}O_5N$), apparently new, was obtained. Hydrolysis of the new alkaloids that were available in sufficient quantity for this purpose yielded, in all cases, retronecine and a new necic acid. A structural formula for senecic acid is proposed.

It has been shown that chemical examination of *Senecio* spp. may be used as an aid to botanical classification.

The chemistry of the alkaloids of *Senecio* species is simplified somewhat by the observation that the basic hydrolytic fragment in most cases consists of retronecine, but it is greatly complicated by the numerous species and by the fact that the acid hydrolytic fragments display an almost bewildering diversity. While there is the strong probability, tantamount to a certainty, that the necic acids are derivatives of terpenes, the presence of two carboxyl and one or more hydroxyl groups, on a carbon skeleton of undetermined nature, does not simplify the rigorous elucidation of structure. It is probable that comparatively large amounts of acids, and therefore alkaloids, will be necessary to solve the structural problems involved, and the investigation described here was initiated with a two-fold end in view. There was the object of finding more convenient sources of known alkaloids, as well as the expectation of finding new ones. In both respects the aims have met with a measure of success.

Senecio integerrimus Nutt. was found to contain two alkaloids. The minor constituent, now termed *integerrimine*, was obtained in only small amounts. It is best represented by $C_{18}H_{25}O_5N$, a formula which is confirmed by the analyses of the fission product. The basic fragment proved to be retronecine. The main constituent was readily obtained in a state of purity. On the basis of analyses, optical rotation, and cleavage products it was definitely

characterized as senecionine (1, 2). The alkaloid, *aureine*, which the author isolated from *S. aureus* (6), proved on direct comparison to be identical with senecionine. Furthermore, an alkaloid now isolated from *S. pseudo-arnica* is also senecionine. It is becoming evident that the last-named is one of the most cosmopolitan of *Senecio* alkaloids, Barger and co-workers having found it in at least three species.

The other plants mentioned in the title, namely, *S. longilobus* Benth., *S. spartioides* T. & G., and *S. ridellii* T. & G., are evidently closely related botanically. In the Index Kewensis they are stated to be identical and synonymous with a prior species, namely, *S. douglasii* D.C., but other authorities are not in agreement with this reduction.* *S. douglasii* was not available for chemical examination but the three species cited yielded results which offer a final answer and they are indeed distinct. The main alkaloid which each elaborates differs from those of the other two, although at least two of the alkaloids are derivatives of retronecine.
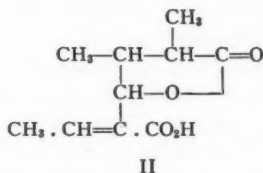
S. spartioides contains a minor alkaloid, termed *spartioidine*, which, on the basis of analytical data only is probably $C_{18}H_{23}O_5N$. The major base is identical with seneciphylline, an alkaloid isolated by Orekhoff (7) and by Konowalowa and Orekhoff (5) from *S. platyphyllus* and from *S. stenocephallus*, respectively. The author is greatly indebted to Professor Orekhoff and Mme. Konowalowa for carrying out an exact comparison with an authentic specimen.

The alkaloid from *S. longilobus*, $C_{18}H_{23}O_5N$, appears to be new and the name *longilobine* is now proposed for it. Hydrolysis yields retronecine and *longinecic* acid, $C_{10}H_{14}O_5$. In the case of *S. ridellii*, the alkaloid *ridelliine*, $C_{18}H_{23}O_6N$, was not available in sufficient quantity to warrant fission experiments. The minor alkaloid already mentioned, namely, spartioidine, was, for the same reason, not hydrolyzed. It is hoped that more material will be available at a future date.

If it be assumed that senecic acid is a derivative of isoprene, a large number of formulae are possible, but when the known facts are taken into consideration a formula with a great degree of probability can be written. These facts are,— (1) The molecule contains two carboxyl groups; (2) one hydroxyl group which lactonizes readily is present and it is therefore in a γ-position to one of the carboxyls; (3) the hydroxyl group is not likely to be in a γ-position with respect to the second carboxyl since two lactones would then be expected, unless, of course, the two lactones, owing to symmetry, would be identical; (4) one double bond and two or three C-methyl groups are present; (5) the double bond is present in the group, $CH_3 . CH{=}C<$, since acetic acid, but not acetone or formaldehyde (formic acid) is formed in the oxidation with

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* *The taxonomic difficulties in the genus Senecio are admittedly enormous. Prof. E. D. Merrill, of Harvard University, was consulted, and he intimated that the Kew "reductions" are not entirely reliable and maintained that structural differences alone were sufficient to allocate specific rank to the cases cited. Sir Arthur Hill, Director of the Royal Botanic Garden, Kew, admitted that a re-examination of the material in the Kew Herbarium disclosed specific differences without, however, explaining the original reduction to S. douglasii. The author is greatly indebted to these authorities for their valuable assistance.*

alkaline permanganate.   Two formulae which account for the above observations are the following—

$$\text{O}\underline{\hspace{3cm}}$$
$$\text{CH}_2\text{—CH—CH—C}=\text{O}$$
$$\qquad\quad \text{CH}_2 \;\; \text{CH}_3$$
$$\text{CH}_3 . \text{CH}=\text{C} . \text{CO}_2\text{H}$$

I

$$\qquad\qquad\quad \text{CH}_3$$
$$\text{CH}_3\text{—CH—CH—C}=\text{O}$$
$$\qquad\quad\;\; \text{CH—O}\underline{\hspace{1cm}}$$
$$\text{CH}_3 . \text{CH}=\text{C} . \text{CO}_2\text{H}$$

II
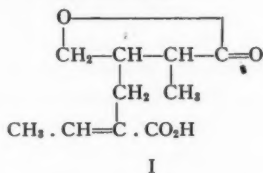
The nitric acid oxidation experiments of Barger and Blackie (1) afford the possibility of distinguishing between these formulae.   The product which they obtained is a lactone and is best represented by the empirical formula $C_6H_8O_4$.   That it is a methyl-paraconic acid of the structure

$$\text{O}\underline{\hspace{3cm}}$$
$$\text{CH}_2\text{—CH}\underline{\hspace{0.5cm}}\text{CH—CO} \quad ,$$
$$\qquad\quad \text{CO}_2\text{H} \;\; \text{CH}_3$$
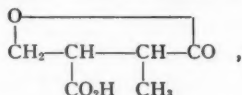
is extremely probable, and its formation from a substance of Formula (I) but not from that of Formula (II) is at once obvious.   An optically inactive form of such an acid has, in fact, been prepared by Fichter and Rudin (4). It was found to melt at 104° C., whereas that obtained by Barger and Blackie melts at 142° C.   These facts, however, do not necessarily prove non-identity. Owing to the presence of two asymmetric carbon atoms, the acid can exist in two racemic and four optically active forms.

Experimental

Senecio integerrimus was collected at Salina Experimental Station, Salina, Utah, in June-July, 1929, and June, 1930.   The plant was mature, seed beginning to form.   *S. longilobus* was collected in Marysvale Canyon, Utah, in September, 1936.   The plants were at and past the flower stage.   *S. spartioides* was collected at Panguitsh Lake, Utah, in September, 1935, and in August, 1936, the collections thus representing the stages of early flower to fruit formation.   *S. ridellii* was collected at Fort Robinson, Nebraska, in August, 1937.   These collections were made by field representatives of the U.S. Department of Agriculture and in all cases were identified by their staff of botanists.   They were made available for chemical study through the kind collaboration of Dr. J. F. Couch of the Pathological Division of the U.S. Bureau of Animal Industry, and the author takes this opportunity to acknowledge his great indebtedness.

The specimen of *S. pseudo-arnica* was presented to the author by Dr. Jacques Rousseau of the Institute Botanique, Université de Montréal.   The specific details for the isolation of *Senecio* alkaloids which the author has outlined in a previous communication (6) have been followed.   In all cases ether extraction of the aqueous acid solution, prepared from the total methanol

extract, yielded fumaric acid. In a number of cases the addition of ammonia to the acidic solution yielded a crystalline precipitate* which, when sufficiently bulky or sparingly soluble in ether, was filtered off and purified separately.

S. integerrimus

The crystalline precipitate from the basified aqueous solution was washed, dried, and recrystallized to constant melting point from chloroform-methanol. It was obtained in stout colourless elongated plates which melted with decomposition at 237° C.† when placed in a bath preheated to 220° C. In admixture with the author's aureine (6) melting at 235° C. there was no depression in melting point. $[\alpha]_D^{28°} = -51.1°$ ($c = 0.4$ in chloroform). The yield was 0.3%. Found: C, 64.28, 64.40; H, 7.46, 7.55; N, 4.47, 4.43%. Calcd. for $C_{18}H_{25}O_5N$: C, 64.46; H, 7.46; N, 4.18%. These data in themselves are sufficient to warrant the supposition that the alkaloid in question is senecionine. Professor Barger, in a private communication, had previously suggested that *aureine* was probably identical with senecionine.

Further confirmation of this identity was obtained from the products of alkaline hydrolysis. The free base (m.p. 118°) and the hydrochloride (m.p. 164°) proved to be identical with retronecine and its hydrochloride. The acidic fragment, in common with the experience of Barger and Blackie, proved to be difficult to purify. The following procedure has, however, proved reliable and the acid can be obtained in good yield.

The dried crude acid was dissolved in chloroform and the solution slowly evaporated to a small volume. Enough benzene to make a thin syrup was added and the solution seeded with a crystal. At this stage crystallization was slow. When apparently complete, the mixture was filtered and washed with benzene. It was recrystallized twice from chloroform-benzene; it then melted not quite sharply at 150–151° C. One recrystallization, however, from boiling benzene in which it is only sparingly soluble, and which left a small amount of oily residue, yielded well developed individual prisms which melted sharply at 154° C. $[\alpha]_D^{25°} = +38.9°$ ($c = 1.28$ in absolute alcohol). These figures are in satisfactory agreement with those recorded for senecic acid lactone.

The observations of Barger and Blackie on nitric acid oxidation were also successfully repeated with this acid, although the yield of crystalline oxidation product was not satisfactory.

Oxidation of Senecic Acid

The lactone (0.7 gm.) was dissolved in hot water and the solution rapidly cooled. Finely powdered potassium permanganate was added at intervals, the temperature being controlled by cooling in running water. An odour of acetaldehyde became perceptible. Addition of permanganate was continued until the pink colour remained for 30 min. The precipitated manganese dioxide was filtered off, the filtrate acidified with hydrochloric acid, and

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* *It is to be observed that this precipitate is contaminated with some inorganic material, the greater portion of which was identified as ammonium magnesium phosphate.*

† *All melting points are corrected.*

distilled to a small volume. The distillate gave completely negative tests for acetone and formaldehyde, but yielded a crystalline precipitate when treated with 2 : 4-dinitrophenylhydrazine. The excessively small amount of the phenylhydrazone did not, however, permit further purification. The main portion of the distillate was titrated to neutrality with standard sodium hydroxide solution and evaporated to dryness. The residue was heated under reflux with an alcoholic solution of the calculated quantity of p-xenacyl bromide. The resulting ester was purified by recrystallization from methanol and obtained in colourless plates melting at 110° C., either alone or in admixture with an authentic specimen of xenacyl acetate (3).

Integerrimine

The combined mother liquor, from which no more senecionine could be crystallized, was largely freed of organic solvents, dilute hydrochloric acid added, and the remainder of the organic solvents was boiled off. The filtered solution was repeatedly extracted with ether. Ammonia was then added and the crystalline precipitate filtered off. A further small amount was obtained from the alkaline filtrate by extracting it with ether. The combined base was dissolved in boiling methanol and the somewhat concentrated solution cautiously diluted with water. The crystalline base was filtered off, washed with dilute methanol, and dried. It was then repeatedly extracted with cold ether and the extracts were evaporated to a small volume. The base which then crystallized melted at 171 to 172° C. It was recrystallized from methanol in which it is readily soluble. As thus obtained *integerrimine* consists of stout prisms melting sharply and without decomposition at 172 to 172.5° C. $[\alpha]_D^{28°} = +4.3°$ ($c = 0.8$ in methanol). Found: C, 64.41, 64.41; H, 7.54, 7.52; N, 4.35, 4.26%. Calcd. for $C_{18}H_{25}O_5N$: C, 64.46; H, 7.46; N, 4.18%. Hydrolysis of integerrimine with alcoholic alkali yielded retronecine and an acid which, when recrystallized from hot water in which it is readily soluble, consisted of colourless prisms melting at 151° C. It is not identical with senecic acid and, since it is probably a new substance, the provisional name, *integerrinecic* acid, is proposed for it. Found: C, 55.57, 55.38; H, 7.38, 7.38%. Calcd. for $C_{10}H_{16}O_5$: C, 55.56; H, 7.41%.

S. pseudo-arnica

There was available only 1500 gm. of the dried material of this species, from which less than 0.3 gm. of total alkaloid could be isolated. It was recrystallized several times from boiling methanol and obtained in colourless elongated plates melting with decomposition at 237 to 238° C. In admixture with a specimen of senecionine from *S. integerrimus*, there was no observable depression in melting point.

S. longilobus

There was available a total of 5.3 kilos. of the dried plant. The alkaloid *longilobine* was recrystallized several times from chloroform-methanol and then consisted of colourless stout prisms melting with decomposition at 217

to 218° C.   For this determination it was placed in a bath preheated to 190°C. and sintering was noticeable at 212 to 215° C.   The yield was 3.1 gm. $[\alpha]_D^{25°} = -79.2°$ ($c = 2$ in 95% ethanol).   Found: C, 64.22, 64.32; H, 7.07, 7.03; N, 4.98, 4.86%.   Calcd. for $C_{18}H_{23}O_5N$: C, 64.86; H, 6.91; N, 4.20%.

The *methiodide* was prepared in methanol and recrystallized first by adding acetone to a concentrated aqueous solution, and then from hot methanol in which it is sparingly soluble.   The fine prisms thus obtained melted at 249° C. to a dark tar.

Hydrolysis of longilobine yielded retronecine (m.p. 118° C.; hydrochloride, m.p. 164° C.) and an acid which was obtained by ether extraction from the acidified hydrolyzate.   The residue from the latter crystallized readily.   It was redissolved in dry ether and the filtered solution evaporated to a thin syrup.   Petroleum ether (40 to 60°) was added until the incipient turbidity just disappeared on mixing.   The addition of a nucleus induced the formation of a hard crust of fine needles in stellate aggregates.   *Longinecic* acid as thus obtained melted to a turbid liquid at 126° C. which became clear at 129° C. There was some slight sintering at a lower temperature and at 150° C. a gas, presumably water, indicating lactone formation, was evolved.   Found: C, 55.38, 55.48; H, 6.64, 6.72%.   Calcd. for $C_{10}H_{14}O_5$: C, 56.08; H, 6.54%.

S. spartioides

A total of 7800. gm. of this plant in the dry condition yielded 42 gm. of crude alkaloid.   The greater portion of this crystallized directly when the aqueous acid solution was basified with ammonia.   The remainder was recovered from the filtrate by ether extraction.   The base was recrystallized from chloroform-methanol and obtained in colourless prisms melting with only slight decomposition at 217° C.   In admixture with longilobine it was completely liquid at 215° C. $[\alpha]_D^{23°} = -119.5°$ ($c = 4.0$ in chloroform). Found: C, 64.46, 64.42; H, 6.74, 6.83; N, 4.63, 4.59%.   Calcd. for $C_{18}H_{23}O_5N$: C, 64.86; H, 6.91; N, 4.20%.

The above constants are in substantial agreement with those of seneciphylline.   Furthermore, hydrolysis yielded retronecine and an acid, recrystallized from ether-hexane, melting at 139° C.   Konowalowa and Orekhoff (5) obtained retronecine and an acid melting at 140° to 141° C. from seneciphylline. Madam Konowalowa kindly determined the melting points of seneciphylline, the alkaloid from *S. spartioides*, and a mixture of the two, simultaneously in a bath preheated to 200° C.   She observed the following melting points, 212° C., 211° C., and 211° C. (uncorrected) respectively.   In addition she prepared the picrates and observed, as before, the respective melting points as 190° C., 189° C., and 190° C. (uncorrected).   The alkaloid in question is therefore identical with seneciphylline.

Spartioidine

The mother liquor from which the seneciphylline had been crystallized was evaporated to remove organic solvents and the residue dissolved in dilute acid.   The filtered solution was repeatedly extracted with ether, then basified

with ammonia, and the resulting crystalline precipitate washed and dried. It was dissolved in hot methanol, and the small amount of seneciphylline which separated on cooling was filtered off. The filtrate on evaporation to a small volume deposited another base which was recrystallized thrice more from hot methanol in which it is moderately soluble. Brilliant stout prisms of *spartioidine* melting sharply and without decomposition at 178° C. were thus obtained (0.1 gm.). Found: C, 64.87, 64.92; H, 6.92, 6.97; N,. 4.74, 4.69%. Calcd. for $C_{18}H_{23}O_5N$: C, 64.86; H, 6.91; N, 4.20%.

The methiodide crystallized directly in colourless fine plates from chloroform–methyl-iodide containing a little methanol. It was washed with the latter solvent and it then melted with decomposition at 239° C.

S. ridellii

The yield of recrystallized base from 120 gm. of material was 0.8 gm. The once-recrystallized substance melted at 196° C. without appreciable decomposition, and further recrystallization did not alter this value. *Ridelline* forms stout well developed prisms sparingly soluble in methanol. Found: C, 61.90, 61.90; H, 6.75; 6.73; N, 4.38, 4.35%. Calcd. for $C_{18}H_{23}O_6N$: C, 61.89; H, 6.59; N, 4.01%.

The *methiodide* prepared in methanol–methyl-iodide crystallized with great facility. It was recrystallized from hot water (sparingly soluble in the cold) and washed with methanol in which it is virtually insoluble; it then melted to a dark tar at 259° C., some darkening taking place at 240° to 245° C.

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THE ALKALOIDS OF *SENECIO* SPECIES

IV. *ERECHTITES HIERACIFOLIA* (L.) RAF.[1]

By Richard H. F. Manske[2]

Abstract

An examination of *Erechtites hieracifolia* (L.) Raf., during which two alkaloids have been isolated, has emphasized the close chemical relation which the genus *Erechtites* bears to *Senecio*. The chief alkaloid, *hieracifoline*, $C_{18}H_{25}O_5N$, on hydrolysis yields retronecine and *hieracinecic* acid. The alkaloid is therefore of the type generally elaborated by *Senecio* species.

Hitherto the genus *Senecio* was the only one in the Compositae Family whose species were known to contain well authenticated alkaloids. The genus *Erechtites* Raf. is closely related taxonomically to *Senecio* and both genera are included in the tribe Senecioneae. It therefore seemed of interest to examine a species of *Erechtites* in order to determine whether the taxonomic similarity had its parallel in alkaloid constituents.

E. hieracifolia (L.) Raf., frequently called the fireweed but entirely distinct from *Epilobium* which is also known by the same common name, is cosmopolitan in eastern North America. A preliminary examination revealed the presence of bases, and although the content is extremely low, it has been possible to isolate two alkaloids in a state of purity. The chief of these is one for which the name *hieracifoline* is proposed. Analytical figures require $C_{18}H_{25}O_5N$, and this observation alone is sufficient to indicate the close relationship to the *Senecio* alkaloids with some of which hieracifoline is isomeric but apparently not identical. Nevertheless the similarity is still further indicated by the nature of the hydrolytic products. The basic fragment proved to be identical with retronecine. The acid, hieracinecic acid, is evidently dibasic.

The second alkaloid is also definitely of the *Senecio* type. The author has for some time made use of Ehrlich's reagent as a diagnosis for *Senecio* alkaloids. They generally melt with decomposition or decompose when heated to 200° to 220° C. The resulting melt gives a positive test for the pyrrole nucleus, an indication that a hydro- or hydroxy-pyrrole is present in the parent base. This test, when applied to the *Erechtites* base melting at 237° C.,* is strongly positive.

Experimental

Hieracifoline

The isolation of the total bases was effected by the procedure recorded in a previous communication (1), namely,— extraction with methanol, extraction of the extract with dilute hydrochloric acid, exhaustion of the filtered aqueous solution with ether**, and finally extraction of the alkaloids from the basified solution with ether.

* *All melting points are corrected.*
** *This ether extract, as in all Senecio spp., yielded an appreciable quantity of fumaric acid.*

The crude alkaloid from *Erechtites hieracifolia* was recrystallized several times from chloroform-methanol and *hieracifoline* was then obtained in large colourless plates melting at 227° C. in a yield of 0.016%. $[\alpha]_D^{26°} = -89.7°$ ($c = 0.4$ in chloroform).   Found: C, 64.49, 64.39; H, 7.25, 7.01; N, 4.40, 4.62%.   Calcd. for $C_{18}H_{25}O_5N$: C, 64.47; H, 7.46; N, 4.18%.

Hydrolysis of Hieracifoline

A suspension of the base (0.9 gm.) in methanolic potassium hydroxide was boiled until it had dissolved.   The methanol was evaporated from the solution, 0.5 cc. water added, and the remainder of the methanol evaporated.   The cooled paste was repeatedly extracted with ether and the combined extract evaporated to a small volume.   Spontaneous crystallization of the characteristic elongated plates of retronecine occurred almost at once.   After filtering and washing with a little ether, the dried base melted sharply at 119° C., either alone or in admixture with an authentic specimen of retronecine. The yield was 0.3 gm.

The alkaline paste from which the retronecine had been extracted was acidified with hydrochloric acid and extracted again with ether.   The residue from the ether extract was treated with a little benzene and warmed gently. The acid which readily crystallized was filtered off and redissolved in a large volume of boiling benzene in which it is only sparingly soluble.   The filtered solution was evaporated to a small volume and the crystals which separated on cooling were filtered off and washed.   As thus obtained the crystals were not well developed.   A product of better appearance was obtained when the acid was dissolved in dry ether, in which it is readily soluble, and the solution evaporated to a thin syrup.   The addition of benzene yielded *hieracinecic* acid in stellate aggregates of fine needles which, when washed with benzene and dried, melted sharply at 132° C.   The melt solidified on slight cooling and then remelted at 131 to 132° C.   Found: C, 55.87, 55.84; H, 7.09, 7.08%.   Calcd. for $C_{10}H_{16}O_5$: C, 55.56; H, 7.41%.

The Minor Alkaloid

The combined mother liquor from the crystallization of hieracifoline was evaporated to a resin and the latter dissolved in dilute hydrochloric acid. The filtered solution was exhausted with ether, basified with ammonia, and the liberated bases were extracted with ether.   The washed extract was evaporated to a small volume and treated with a little methanol.   The crystals which had separated in the course of several days were filtered off and recrystallized several times from chloroform-methanol.   The *base* then consisted of hard stout prisms, with pointed terminations, which melt with decomposition at 237° C.   Senecionine (2) melts at the same temperature but a mixture of the two was liquid at 216 to 220° C.   The yield was about 0.003%.   Found: C, 65.04, 65.00; H, 4.77, 4.65; N, 3.72, 3.82%.   Calcd. for $C_{20}H_{19}O_6N$: C, 65.04; H, 5.15; N, 3.79%.   Calcd. for $C_{20}H_{17}O_6N$: C, 65.39; H, 4.63; N, 3.81%.

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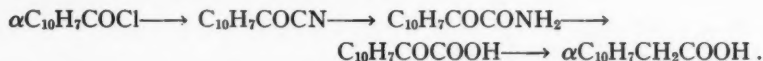2. MANSKE, R. H. F.   Can. J. Research, B, 17 : 1-7.   1939.

SYNTHESIS OF NAPHTHYL-ACETIC ACID[1]

By A. Cambron[2]

Abstract

A simple and convenient method[*] for the preparation of α-naphthyl-acetic acid from readily obtainable starting materials is described.

A convenient method for the preparation of α-naphthyl-acetic acid has become of particular interest since Zimmerman and Wilcoxon (16) reported that this acid possessed properties similar to those of indole-acetic as a plant growth promoter or for initiating root formation.

Boessneck (4), who was the first to synthesize α-naphthyl-acetic acid, obtained it by the following procedure:

$$\alpha C_{10}H_7COCl \longrightarrow C_{10}H_7COCN \longrightarrow C_{10}H_7COCONH_2 \longrightarrow$$
$$C_{10}H_7COCOOH \longrightarrow \alpha C_{10}H_7CH_2COOH .$$

Other methods of synthesis were later reported by Tiffeneau and Daudel (14, p. 679), who used the Grignard reaction between 1-bromo-naphthalene and acetaldehyde; by Weitzenböck and Lieb (15, p. 556), who prepared the intermediate α-naphthyl-acetamide by the action of ammonium sulphide on methyl-α-naphthyl ketone; and by several other chemists, who followed various procedures (2, p. 205; 8,9).

The first simple method reported in the literature is that described by Mayer and Oppenheimer (11, p. 2139) and later used by Zimmerman and Wilcoxon (16) and by Olivier and Wit (12). This method consists in brominating α-methyl-naphthalene at a temperature of 200° C., and converting the bromo-methyl-naphthalene to the nitrile, which is then hydrolyzed to the acid:

$$C_{10}H_7CH_3 \longrightarrow C_{10}H_7CH_2Br \longrightarrow C_{10}H_7CH_2CN \longrightarrow C_{10}H_7CH_2COOH .$$

Attempts to duplicate the experiments of Mayer and Oppenheimer (11, p. 2139) did not at first yield satisfactory results. This was later found to be due to the fact that the bromination was being carried out in the dark in an enclosed electrically heated air bath. The original authors very probably operated in a vessel exposed to direct or diffused sunlight. Their method was considerably improved by carrying out the reaction in a Pyrex flask irradiated by a carbon arc, the yield of bromide obtained under these conditions being 59% of the theory as compared to a yield of 43.5% reported by them. This observation was confirmed in a report published shortly afterwards by Olivier and Wit (12), who carried out the same reaction in quartz glass irradiated by a mercury lamp. These authors, however, reported a yield of bromide of only 32%.

The above method suffers from a serious disadvantage in that α-methyl-naphthalene is a costly material, and, furthermore, is difficult to obtain free from the β-isomer.   Consequently, an alternative method for the production of the required halogen-substituted α-methyl-naphthalene was investigated.   This method is based on a reaction first observed by Grassi and Maselli (7), who reported the formation of benzyl chloride by the action of s-dichloromethyl ether, formed by the action of hydrochloric acid on formaldehyde, on benzene.   Blanc (3) used the same reaction for the preparation of chloromethyl-naphthalene and reported a yield of 54% based on the naphthalene used, but Anderson and Short (1), who followed Blanc's procedure, obtained a yield of only 11%.   By modification of Blanc's procedure, however, the yield was raised to 42%.

A modification of the above method for the preparation of chloromethyl-naphthalene is described in D.R.P. 533,132.   The method was later used by Rupe and Brentano (13), and by Coles and Dodds (5).   The procedure described in the above patent consists in treating a mixture of naphthalene, 30% formaldehyde, and concentrated hydrochloric acid with concentrated sulphuric acid at 60° C., the sulphuric acid being added in the course of a few hours and the reaction mixture being then kept at 60°, with good stirring for about 20 hr.

A further modification of the same method was described by Darzens and Lévy (6).   Their method consists in adding an excess of gaseous hydrochloric acid to a suspension of paraform in glacial acetic, then reacting the solution of s-dichloromethyl ether thus formed with an equimolecular proportion of naphthalene, no condensing agent being used.   Their procedure requires a heating period of 20 hr.   They claimed a yield of 71.5%, based on naphthalene.   An attempt to duplicate their experiment did not confirm this claim, the highest yield obtained being 31.6%.   It was found, however, that by the use of essentially the same procedure as that described by these authors, the yield of chloride could be increased to 45% by using phosphoric acid as a condensing agent, and, further, that under these conditions the time of reaction was reduced to about 10 hr.   The time required for completing the reaction was further reduced by using aqueous concentrated hydrochloric and by increasing the temperature from 60° to 98°–100° C.   The yield of chloride under these conditions is 56.5% of theory, based on the total naphthalene used, and 67% based on naphthalene reacted, the reaction being completed in $4\frac{1}{2}$ hr.

The second step in the synthesis of α-naphthyl-acetic acid, when the starting material is chloro- or bromo-methyl-naphthalene, is the conversion of the halogen compound to the corresponding nitrile.   This is effected by the known method of refluxing the halogen compound with an alcoholic solution of potassium cyanide.

The third and final step in the synthesis is the hydrolysis of the nitrile. Mayer and Oppenheimer (11, p. 2139) describe a method for the hydrolysis of α-naphthyl-acetonitrile by refluxing with potassium hydroxide in the

presence of hydrogen peroxide. The same method has been used by Olivier and Wit (12) who found, however, that the presence of the peroxide was not only superfluous but diminished the yield. The latter authors report that attempts to effect the hydrolysis of the nitrile by the action of phosphoric acid were unsuccessful, owing to the decomposing action of the acid on the product.

The present author has found that the hydrolysis of the nitrile by the action of alkalis, whether carried out with or without the addition of hydrogen peroxide, yields a product extremely difficult to purify, several recrystallizations being required before it is obtained in a satisfactory state of purity. It was found, however, that the hydrolysis could be carried out more conveniently and a more easily purified product obtained by effecting the hydrolysis with a mixture of equal volumes of sulphuric acid, acetic acid, and water.

R. H. F. Manske and A. E. Ledingham, of these laboratories, have done further work on the present synthesis of naphthyl-acetic acid, particularly with the object of identifying the by-products formed in the various stages of the synthesis (10).

α-Chloromethyl-naphthalene   **Experimental**

A mixture of paraform (90 gm.), naphthalene (288 gm.), acetic acid (250 gm.) concentrated hydrochloric acid (280 cc.), and syrupy phosphoric acid (135 cc.) was heated at 98 to 100° C. for 4½ hr. with good stirring. The reaction mixture was then poured into two litres of cold water, the product being obtained in the form of an oil heavier than water. The product was washed by stirring two or three times with two litres of water, and decanting the aqueous layer. The oil was then filtered from a small amount of an insoluble by-product and distilled under reduced pressure. Yields: 223 gm. of a product boiling at 145° to 160° C. at 6 to 8 mm.; 56.5%, based on naphthalene used.

α-Naphthyl-acetic acid

The chloromethyl compound was first converted to the nitrile. α-Chloromethyl-naphthalene (223 gm.) was refluxed for an hour with a solution of potassium cyanide (110 gm.) in ethyl alcohol (500 cc.) and water (200 cc.). The alcohol was distilled off, the product washed with water, filtered from water insoluble solids, dried under reduced pressure, and distilled, the fraction boiling at 175 to 185° at 11 to 14 mm. being collected.

The acetonitrile was hydrolyzed by refluxing with a mixture of sulphuric acid (350 cc.), acetic acid, (350 cc.), and water (350 cc.), at 120 to 125° for 45 min. The crude acid was then precipitated by pouring the reaction mixture in three litres of cold water with good stirring. The acid was purified by dissolving in 50% alcohol, treating the boiling solution with charcoal, and precipitating the acid by dilution with cold water; yield, 131.5 gm. of α-naphthyl-acetic melting at 131.5°. This represents an over-all yield of 31.5%, based on the naphthalene used.

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A SYNTHESIS OF α-NAPHTHYL-ACETIC ACID AND SOME HOMOLOGUES[1]

By Richard H. F. Manske[2] and Archie E. Ledingham[3]

Abstract

In the course of a study of the synthesis of α-naphthyl-acetic acid, a method was elaborated by Dr. A. Cambron that made available large quantities of α-chloromethyl-naphthalene. During the purification of the crude product and in the later stages of the synthesis we have encountered a number of by-products. Among others, these include methyl α-naphthyl-methyl ether, di-α-naphthyl-methyl ether, α-naphthyl carbinol, and 1 : 5-bis-chloromethyl-naphthalene. The last-named was converted into 1 : 5-naphthylene-diacetic acid, m.p. 280° C., via the corresponding nitrile. δ-(1-Naphthyl)-valeric acid, m.p. 84° C., and ε-(1-naphthyl)-hexoic acid, m.p. 62° C., were synthesized by standard procedures.

The observation of Zimmerman and Wilcoxon (12), that α-naphthyl-acetic acid possesses properties similar to those of indolyl-3-acetic acid in initiating certain responses in plants, has aroused some interest in its further chemical study as well as in procedures designed to render it readily accessible (4, 9, 11).

The obvious starting material is α-chloromethyl- or α-bromomethyl-naphthalene. The subsequent stages involving the preparation and hydrolysis of the corresponding cyanide would not be expected to offer serious difficulties. While the bromination of α-methyl-naphthalene, particularly in the light of a mercury vapour lamp, proceeds moderately well (8), some nuclear bromination is certain to occur, and the elimination of the halogen from the final product is difficult.

A number of procedures for the preparation of α-chloromethyl-naphthalene from naphthalene, formaldehyde, and hydrogen chloride have been published recently (1, 2). The reaction involved is an extension of that used by Stephen, Short, and Gladding (10) and involves only a change of condensing agents and modified temperatures. Dr. A. Cambron (see preceding paper), of these laboratories, has made a study of this condensation, and the crude α-chloromethyl-naphthalene which he has obtained was kindly placed at our disposal for further study. On careful fractionation it yielded a product which consisted very largely of the α-isomer, although we have reason to believe that a small amount of the β-isomer is present and prevented the complete crystallization of our purest distillate. A higher boiling fraction consisted of a readily crystallizable mixture from which apparently-pure 1 : 5-bis-chloromethyl-naphthalene has been obtained. Anderson and Short (1) have established the orientation of this compound, and our observations fully confirm theirs. Admixed with the crude product are probably isomeric bis-chloromethyl-naphthalenes as well as a small amount of α-naphthyl-carbinol. The latter

presumably arises from the hydrolysis of the chloride. It was isolated in the course of purification of the dicyano-compound prepared from the dichloro-compound. The former was hydrolyzed to naphthylene-1 : 5-diacetic acid. The orientation of this acid was established by conversion to 1 : 5-dimethyl-naphthalene by heating the potassium salt with soda-lime.

A number of by-products were encountered when the α-chloromethyl-naphthalene was converted to α-naphthyl-acetic acid. The nitrile was accompanied by a somewhat more volatile non-nitrogenous liquid which proved to be methyl-α-naphthyl-methyl ether. The higher boiling fraction contained some α-naphthyl-acetamide and di-α-naphthyl-methyl ether. Both of the ethers are regarded as the result of the action of the alkali contained in the cyanide on the chloride, and the methyl ether owes its presence to the use of methanol as solvent. It is a liquid which yields a well crystallized picrate, whereas the symmetrical ether is a crystalline solid.

Hydrolysis of the nitrile in alkaline solution is rather slow. Hydrolysis with sulphuric acid in slightly diluted acetic acid yields an acid contaminated with some of the amide and a neutral nitrogenous substance, the nature of which is still obscure. Analytical figures indicate $C_{24}H_{21}ON$ or a lower homologue, but in either case the hydrogen content is too large to be accounted for by condensation and elimination reactions alone.

We have prepared a homologous series of ω-(1-naphthyl)-aliphatic acids up to and including ε-(1-naphthyl)-hexoic acid, in order to observe their effect on plant growth. Dr. N. H. Grace has this problem under study and will report upon it shortly. It may be mentioned, however, that all members of the series show some activity as phytohormones.

The propionic and butyric acids were prepared by published methods, and for the synthesis of the valeric and hexoic acids we condensed the appropriate ω-(1-naphthyl)-alkyl bromides with sodio-malonic ester. The bromides were obtained from the corresponding alcohols and these in turn were prepared by the Bouveault reduction. For practical purposes these syntheses reach their limit in the hexoic acid, the salts of which possess the properties of soaps. With the higher homologues the yields in the malonic ester synthesis are materially reduced, and the alcohols are convertible into bromides only with difficulty. Even the crystallization of the final products is by no means facile, and the melting points (61° C. for the hexoic acid) fall rapidly with increase in chain length.

Experimental

α-Chloromethyl-naphthalene

The crude α-chloromethyl-naphthalene obtained from Dr. Cambron was fractionated *in vacuo*; it yielded a forerun of unchanged naphthalene and then the main fraction of the chloro-compound distilling at 148 to 150° C. (14 mm.). It finally crystallized for the greater part, and the isolated crystals melted sharply at 32° C.* There was present a small amount of oil which could not be separated by distillation alone, but it, too, solidified completely on cooling

* *All melting points are corrected.*

to 0° C.   It is probable that the liquid is a mixture containing a small amount of β-chloromethyl-naphthalene.

1 : 5-Bis-chloromethyl-naphthalene

The high boiling residue from the fractionation of the α-chloro-compound crystallized for the greater part on cooling. It was transferred to a short necked flask, and the fraction boiling at 175 to 185° (12 mm.) collected separately. The distillate was recrystallized twice from hot benzene and was obtained in colourless prisms melting at 144° C.   Calcd. for $C_{12}H_{10}Cl_2$:   C, 64.02; H, 4.45; Cl, 31.53%.   Found: C, 64.42; H, 4.58; Cl, 31.47%.

Naphthylene-1 : 5-diacetonitrile†

A solution of crude 1 : 5-bis-chloromethyl-naphthalene (85 gm.) in 150 cc. of dioxane was added to potassium cyanide (55 gm.) in 50 cc. of water, and the mixture heated on the steam bath for 24 hr.   The resulting dicyano-compound was isolated by extracting the diluted mixture with benzene. The benzene solution was filtered to remove some suspended material and washed with dilute acid and with water.   Removal of the benzene yielded an oil which was distilled under reduced pressure.   The low boiling fraction (up to 200° C. at 2 mm.) yielded some α-naphthyl-carbinol (*vide infra*). The main fraction, b.p. 200 to 235° (2 mm.) mostly at 230° C. (2 mm.), crystallized readily.   It was washed once with methanol and redissolved in chloroform-acetone.   The somewhat concentrated solution yielded, on the addition of methanol, colourless fine needles of naphthylene-1 : 5-diaceto-nitrile melting at 140° C.   Calcd. for $C_{14}H_{10}N_2$: C, 81.55; H, 4.85; N, 13.59%. Found: C, 81.50; H, 5.06; N, 13.46%.

Naphthylene-1 : 5-diacetic Acid

A mixture of naphthylene-1 : 5-diacetonitrile (5 gm.), sulphuric acid (21 gm.), acetic acid (24 gm.), and water (8 cc.) was heated in a flask fitted with a stirrer.   After 5 to 10 min. at 100° to 110° C. the heterogeneous mixture became clear and in about 45 min. crystals began to separate.   After one hour the mixture was diluted with water, and the sand coloured crystals were filtered off and washed.   The acid was purified by solution in alkali and repre-cipitation with acid and finally by recrystallization from hot methanol in which it is sparingly soluble.   As thus obtained naphthylene-1 : 5-diacetic acid consists of fine colourless needles melting at 280° C.   Calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.92%; Equiv. 244.   Found: C, 68.84; H, 5.11%; Equiv. 246.

A small amount of the crude acid was decarboxylated by heating the potassium salt with soda-lime in a stream of nitrogen.   The distillate was collected in ether and the washed and filtered solution evaporated.   The residual oil was converted to a picrate in methanol solution and recrystallized from hot methanol.   The stout bright orange prisms thus obtained melted at 138° C.; this is the melting point recorded for the picrate of 1 : 5-dimethyl-naphthalene (1).

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† *In conformity with the term phenylene for the disubstituted benzene derivatives, the term* naphthylene *is used for the disubstitution products of naphthalene.*

α-Naphthyl-carbinol

The low boiling fraction from the preparation of the dinitrile on extended hydrolysis with methanolic potassium hydroxide yielded some naphthylene-1 : 5-diacetic acid and a neutral oil which was extracted from the alkaline solution with benzene. It was distilled *in vacuo* and the main fraction, b.p. 143 to 145° (2 mm.), which solidified on cooling was recrystallized from benzene-hexane. The colourless needles thus obtained melted at 64° C. and in admixture with a specimen of α-naphthyl-carbinol, prepared as described below, there was no depression in melting point. Calcd. for $C_{11}H_{10}O$: C, 83.54; H, 6.33%. Found: C, 83.49; H, 6.58%.

The carbinol in question was prepared from α-chloromethyl-naphthalene as follows: a solution of the latter (35 gm.) and potassium acetate (25 gm.) in acetic acid (70 gm.) was heated under reflux for two hours. Benzene was added and the mixture washed with water. Evaporation of the benzene and distillation of the residue yielded *α-naphthyl-carbinyl acetate* as a colourless thin oil boiling at 134 to 136° (1.5 mm.). This was hydrolyzed with alcoholic potassium hydroxide and the unsaponifiable oil extracted with benzene. The benzene was removed *in vacuo* and the residue distilled. The fraction boiling at 140 to 143° (1.5 mm.) crystallized immediately when inoculated with a specimen of α-naphthyl-carbinol obtained as described above. Two recrystallizations from benzene-hexane yielded colourless needles melting at 63° C. The over-all yield was 80 to 90% of the theoretical.

α-Naphthyl-acetonitrile

A mixture of sodium cyanide (80 gm.), water (100 cc.), α-chloromethyl-naphthalene (205 gm.), and methanol (400 cc.) was heated under reflux for one hour. The cooled mixture was diluted with water and extracted with benzene. The residue, after the removal of the solvent, was distilled and the fraction boiling at 140 to 160° (1 mm.) collected. The yield was uniformly 180 gm.

Large quantities of the crude nitrile were redistilled through a long column, and the pure nitrile was obtained as a colourless oil boiling at 150 to 152°C. (1.5 mm.) in yields approximating 85%.

Methyl α-Naphthyl-methyl Ether

The low boiling fraction from the preparation of α-naphthyl-acetonitrile was refractionated several times and ultimately obtained as a colourless oil boiling at 101 to 103° C. (1.5 mm.). Analyses indicate that this substance is methyl α-naphthyl-methyl ether. Calcd. for $C_{12}H_{12}O$: C, 83.71; H, 6.98%. Found: C, 83.69; H, 7.00%.

The *picrate* was recrystallized from methanol and obtained in yellow needles melting at 95° C. Calcd. for $C_{22}H_{21}O_7N$: N, 10.47%. Found: N, 10.37%.

Di-α-naphthyl-methyl Ether and α-Naphthyl-acetamide

The high boiling fraction from the preparation of α-naphthyl-acetonitrile was obtained as a pale yellow oil boiling at 175 to 185° C. (1.5 mm.). This

in contact with acetone-methanol yielded a copious crop of crystals.   The
product was redissolved in chloroform-methanol and the filtered solution
evaporated to a small volume.   Crystallization followed the addition of
methanol and the substance (m.p. 118° C.), when recrystallized again from
chloroform-methanol, was obtained in uniform stout parallelepipeds, the
angles approaching 90°, melting sharply at 121° C.   Analyses prove this
substance to be *di-α-naphthyl-methyl ether*.   Calcd. for $C_{22}H_{18}O$: C, 88.59;
H, 6.04%.   Found: C, 88.55; H, 6.17%.

The filtrate from the first recrystallization of the above-described ether was
evaporated to a small volume and cooled.   The crystalline product which
separated was recrystallized twice from hot methanol, and obtained in long
stout prisms melting at 184° C.   Recrystallization from much hot water
did not change the melting point.   It contains nitrogen and undoubtedly
consists of α-naphthyl-acetamide which has been described by Bössneck (3)
as melting at 180 to 181° C. (? corr.).

α-Naphthyl-acetic Acid

α-Naphthyl-acetonitrile is conveniently hydrolyzed by the following pro-
cedure, the essential features of which were suggested to us by Dr. Cambron.
A mixture of the nitrile (70 gm.), sulphuric acid (150 gm.), water (54 cc.) and
acetic acid (100 cc.) in a long necked flask is stirred and slowly heated to 110 to
115° C., at which temperature a mild exothermal reaction sets in and a homo-
geneous solution results.   Stirring with heating just to the boiling point is
continued for one hour, during which the mixture becomes heterogeneous
again.   A little water is added and the whole is poured into a large volume of
water with vigorous stirring.   The filtered, washed, and dried product is
obtained in a yield of 95 to 98% of the theoretical.   Preliminary purification
can be effected by dissolving in aqueous ammonia and reprecipitating with
acid.

A neutral nitrogenous substance, insoluble in ammonia, was encountered
at this point.   It was partly purified by heating with alcoholic potassium
hydroxide, during which process some ammonia was evolved. It is probable that
the latter resulted from the hydrolysis of some α-naphthyl-acetamide, since the
corresponding acid could be obtained from the alkaline solution.   The in-
soluble residue was recrystallized twice from chloroform-methanol, once from
dioxane-acetone, and finally from dioxane in which it is moderately soluble
only when hot.   The fine, apparently homogeneous, needles thus obtained
melted at 179° C.   The substance contains nitrogen, and analyses indicate
the formula $C_{23}H_{19}ON$ or $C_{24}H_{21}ON$.   Oxidation with chromic acid in acetic acid
yielded no definite product.   Found: C, 84.30, 84.15; H, 5.97, 5.98; N, 3.98,
4.13%.   Calcd. for $C_{24}H_{21}ON$: C, 84.96; H, 6.19; N, 4.13%.

Complete purification of α-naphthyl-acetic acid is conveniently effected by
partial precipitation from an alkaline solution, the first small portion being
rejected.   Subsequent recrystallization from water and then from benzene
yields the acid in dense stout prisms melting at 134° C.   When this product

is recrystallized again from water it melts at 132° C., presumably owing to the occlusion of small amounts of water.

The methyl ester boils at 168 to 170° (2 mm.).

δ-(1-Naphthyl)-valeric Acid

The β-(1-naphthyl)-propionic acid required for the synthesis of the valeric acid was prepared from α-chloromethyl-naphthalene and sodio-malonic ester. It possesses the properties recorded by Meyer and Sieglitz (6). The methyl ester melts at 36° C. and is the only crystalline ester which has been encountered in the homologues of α-naphthyl-acetic acid. It boils at 145° (1 mm.).

Reduction of the ester with sodium and alcohol (5) yielded γ-(1-naphthyl)-propanol as a faintly yellow oil boiling at 145° (1 mm.) in 70% of the theoretical. This was converted into the bromide in a yield of 70 to 75% by the following procedure, which was also used to convert β-(1-naphthyl)-ethanol and δ-(1-naphthyl)-butanol into the corresponding bromides.

The alcohol was alternately saturated with gaseous hydrogen bromide and heated on a steam bath, until the necessary increase in weight was obtained. Toward the end of the reaction a few drops of sulphuric acid may be added to advantage. The mixture was diluted with benzene and washed with sulphuric acid until the acid layer was virtually colourless. The benzene solution was then washed with 10% sodium chloride solution, and the solvent finally distilled. The residue was distilled *in vacuo* and 3-(1-naphthyl)-1-bromopropane obtained as a colourless oil boiling at 153 to 155° (3 mm.).

Condensation of the bromide with sodio-malonic ester was effected in boiling absolute ethanol and the substituted malonic ester isolated by extracting with benzene and washing with water. In this case, as in those concerned with the synthesis of the butyric and hexoic acids, distillation of the malonic ester was unsatisfactory, owing to the large amount of unsaponifiable high boiling resin formed during the malonic ester condensation. The solvent was therefore removed and the residue hydrolyzed with alcoholic potassium hydroxide. The alcohol was boiled out of the diluted solution, and the aqueous solution extracted with benzene to remove resin. It was filtered and acidified with hydrochloric acid. The oily malonic acid derivative crystallized eventually. It was filtered off, decarboxylated at 190 to 200° C. and the cooled melt recrystallized from benzene and then from benzene-hexane. Fine colourless needles of δ-(1-naphthyl)-valeric acid melting at 89° C. were obtained in a yield of 20 to 25% based on the bromide taken. Calcd. for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02%. Found: C, 77.75; H, 8.53%. The methyl ester, b.p. 153 to 155° (3 mm.), was obtained only as an oil.

ε-(1-Naphthyl)-hexoic Acid

β-(1-Naphthyl)-ethanol was converted into the bromide, by the procedure outlined above, which was obtained in a yield of 73% of the theoretical. It boils at 135 to 138° (1.5 mm.). Its purity was checked by a bromine analysis. (Calcd. for $C_{12}H_{11}Br$: Br, 34.0%. Found: Br, 33.4%). Condensation with

sodio-malonic ester, leading ultimately to the synthesis of γ-(1-naphthyl)-butyric acid, was carried out by the procedure recorded by Schlenk, Bergmann, and Bergmann (8).   The acid was obtained from benzene in elongated plates melting at 112° C. in an over-all yield of 58% based on the bromide used.

The methyl ester is an oil boiling at 152 to 155° (0.5 mm.).

Reduction of the methyl ester of γ-(1-naphthyl)-butyric acid in absolute ethanol with sodium (5) gave an 83% yield of δ-(1-naphthyl)-butanol as a colourless oil boiling at 150 to 155° (0.5 mm.).   The bromide was obtained from it as a colourless oil boiling at 160 to 163° (2 mm.) in a yield of 39% of the theoretical.

The conversion of the 4-(1-naphthyl)-1-bromobutane into ϵ-(1-naphthyl)-hexoic acid was effected as in the case of the lower homologue.   The corresponding malonic acid did not crystallize and several weeks elapsed before a crystal nucleus of the mono-basic acid was obtained.   It was then possible to recrystallize it from hexane in which it is moderately soluble.   The purified acid melts at 62° C. and consists of small colourless prisms   The yield, based on the bromide, was 20 to 25%.   Calcd. for $C_{16}H_{18}O_2$: C, 79.34; H, 7.44%. Found: C, 77.98; H, 8.82%.

An aqueous alkaline solution of the acid exhibits a slight opalescence and foams like a soap solution.

Acknowledgment

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THE OCCURRENCE OF *l*-NICOTINE IN *ASCLEPIAS SYRIACA* L.[1]

By Léo Marion[2]

Abstract

The root of *Asclepias syriaca* L., contains an alkaloid which has been identified as *l*-nicotine. The base was characterized via its picrate and picrolonate.

The Australian plant *Duboisia hopwoodii*, belonging to the natural family Solanaceae, is the only well established source of *l*-nicotine (3) which has been found extraneous to the *Nicotiana* spp. Preobraschensky (2) claimed to have found nicotine in *Cannabis sativa*, a plant belonging to the family Urticaceae. Some doubt has been cast on this work by Siebold and Bradbury (4), who re-examined the plant and obtained a basic oil apparently different from nicotine. They assigned the name cannabinine to this base, although they did not characterize it further. The occurrence of *l*-nicotine in *Asclepias syriaca* L., a milkweed of widespread distribution, is now placed on record. This plant belongs to the Asclepiadaceae. Owing to the presence of nicotine in *A. syriaca*, a plant which is quite remote from the *Nicotiana* spp., it would seem that the claim of Preobraschensky should not be too lightly dismissed, and that it could be discredited only after a rigorous investigation of *Cannabis sativa*.

The root of *Asclepias syriaca* L., was found to contain a small quantity (0.001%) of an oily base which could be distilled to a colourless oil having a strong odour of nicotine. It was characterized by means of its picrate and its picrolonate, the melting points of which were determined before and after admixture with the corresponding compounds prepared from an authentic specimen of *l*-nicotine.

Besides *l*-nicotine, the methanolic extract of the plant was found to contain fumaric acid and a substance, m.p. 190° C.*, which yielded analytical figures in good agreement with $C_{16}H_{26}O$. This substance may be identical with *Asclepion*, isolated in an impure condition by List (1) from the milky sap of the plant.

Experimental

The roots of *Asclepias syriaca* L. (23 kilos), collected in the neighbourhood of Ottawa, were dried, ground and extracted in Soxhlets with methanol. The solvent was largely distilled from the extract, and the residue heated on the steam bath with water slightly acidified with acetic acid. After the insoluble material had been filtered off, the filtrate was basified with potassium hydroxide and distilled in steam under reduced pressure. The distillate was acidified with a little hydrochloric acid, concentrated under reduced pressure

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* *All melting points are corrected.*

to about 500 cc., filtered, and strongly basified with saturated aqueous potassium hydroxide. The basic solution was extracted repeatedly with ether and the combined ethereal extracts were distilled on the steam bath to remove the solvent. A dark brown oil was left.

Isolation of l-Nicotine

The dark brown basic oil was distilled *in vacuo* and an oil collected which was redistilled at 85° (1 mm.). Wt., 0.21 gm. (yield, 0.001%). About one-half of the oil was converted to a picrate which was recrystallized from boiling methanol as yellow needles, m.p. 228°. Calcd. for $C_{22}H_{20}O_{14}N_8$: C, 42.58; H, 3.22; N, 18.06%. Found: C, 42.79; H, 3.25; N, 17.97%. Admixture with an authentic specimen of *l*-nicotine dipicrate (m.p. 228°) did not depress the melting point. The remainder of the oil was dissolved in aqueous acetone and treated with the calculated quantity of picrolonic acid. The crystalline picrolonate, after recrystallization from boiling acetone, melted at 228°, either before or after admixture with authentic *l*-nicotine dipicrolonate.

Isolation of Fumaric Acid

Some of the aqueous solution which had been steam distilled was acidified with hydrochloric acid and extracted with ether. The ethereal extract yielded an acid which, after several recrystallizations from water, melted at 295°. Admixture with fumaric acid failed to lower the melting point.

Isolation of a Neutral Substance

When the root was extracted in a percolator with cold methanol, and the extract slightly concentrated *in vacuo*, a crystalline substance was gradually deposited from the cooled methanolic solution. This substance was purified by several recrystallizations from a mixture of ethyl acetate and methanol. The colourless crystals, which were deposited in stellar aggregates, melted at 190° C. Calcd for $C_{16}H_{26}O$: C, 82.01; H, 11.11%. Found: C, 82.10, 82.00; H, 11.13, 11.16%.

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VAPOUR-PHASE CRACKING OF GAS-OIL IN BAFFLED METAL TUBES[1]

By Adrien Cambron[2] and Colin H. Bayley[2]

Abstract

The vapour phase cracking of a gas-oil fraction has been investigated under conditions of turbulent and streamline vapour flow. The results show that the increased rate of heat transfer and the more uniform temperature distribution brought about by turbulence cause a very marked increase in the amount of low boiling liquids and olefines produced at the lower temperatures, particularly in the range 600 to 700° C. The character of the vapour flow was also found to have a marked influence on the composition of the liquid products, there being considerably more aromatics produced, especially at the higher temperatures, under conditions of highly turbulent flow.

At 600 and 650° C., for instance, 8.4 and 16.1% of the gas-oil put through was recovered as 205° end-point gasoline when an empty tube was used. However, when a baffled tube was employed, the yield of 205° end-point gasoline was 16.0 and 22.4% respectively, under the same conditions of temperature and liquid rates.

At 800° C. about 23% of the gas-oil put through was recovered as 205° end-point gasoline when either the empty or the baffled tube was used. In the latter experiments, however, 40% of the gasoline consisted of benzene and 20% of toluene, while in the former, the gasoline contained only about 15% of benzene and 5% of toluene.

Experiments have been carried out in which a fraction of the off-gas was recirculated, with the entering gas-oil vapours, through the cracking furnace. Such a procedure did not increase the yield of gasoline, and apparently decreased the yield of aromatics.

The vapour-phase cracking of heavy petroleum fractions first became of technical interest during the Great War (9, 11) when attempts were made to utilize the process for the production of aromatics, particularly toluene. It has been stated (5), however, that the complexity of the products obtained by a process such as Hall's, for instance, rendered the isolation of the lower aromatics commercially impractical, especially when toluene could be extracted in large quantities from Borneo petroleum.

Although a considerable amount of work has been done on the subject of vapour-phase cracking, the results of only a few investigations have been published. Geniesse and Reuter (6, 7) determined the relation between temperature and rate of cracking of gas-oil, and showed that long times of contact at low temperatures gave essentially the same amount of cracking as short times of contact at high temperatures. These authors also determined the independent effect of the time and temperature factors on the yield and the composition of the gasoline and of the fixed gases produced. The highest temperature used by the above-mentioned authors was 700° C. Groll (8) investigated the vapour-phase cracking of gas-oil and of other heavy fractions over a wider temperature range, using temperatures up to 850° C. Groll used

metal reaction tubes, and most of his experiments were carried out in the presence of steam.   His results confirmed Geniesse and Reuter's conclusions that the composition and the yield of the products are functions of temperature and time of contact, and an attempt was made to determine the nature of this function in the case of a given charging stock.

A growing demand for high antiknock fuels, resulting from the use of increasing compression ratios by the automobile industry, has in the last few years caused a revival of interest in the vapour-phase cracking of heavy hydrocarbons.   Several difficulties, however, have retarded the development of vapour-phase processes.   Of these difficulties the most important are: (i) the high olefine content of the cracked distillate, which causes considerable losses on refining; (ii) the hydrocarbon loss due to the formation of fixed gases; and (iii) the low rates of throughput as compared with liquid-phase processes, this being due primarily to the fact that the rate of heat transfer from heating surface to vapour is considerably lower than the rate of heat transfer to a liquid.

The first of the above difficulties has been largely overcome by the use of special activated clays for the refining of the raw vapour-phase distillates. By the use of these clays the reactive gum-forming di-olefines are removed, whereas the mono-olefines are not, and appear as valuable antiknock constituents in the refined distillate.

With regard to the formation of fixed gases in vapour-phase processes, an apparently successful attempt has been made to reduce the losses due to gas formation by polymerizing the olefines present in these gases to liquids, and it is stated that improvements in the vapour-phase process, together with the increased gasoline yields due to the polymerization operation, now permit this process to compete favorably with the liquid-phase cracking process (10). Besides their possible use for the production of gasoline, vapour-phase cracking gases, which contain a high concentration of the lower olefines, are becoming increasingly important as a raw material for the production of industrial organic chemicals.

It has been shown (1, 3) that the pyrolysis of gaseous paraffins can be carried out at considerably higher space velocities under conditions of highly turbulent gas flow, as induced by the use of specially designed baffles, owing to the marked increase in the rate of heat transfer from tube wall to gas under these conditions.   As a further consequence of the use of baffled tubes, the liquid products obtained under conditions of highly turbulent flow are much less complex than the products obtained when the pyrolysis of the lower paraffins is carried out under normal flow conditions, the more uniform temperature distribution in the reaction zone under the former conditions tending to suppress side reactions.   The object of the present investigation was primarily to determine whether the vapour-phase cracking of heavy petroleum fractions in baffled tubes would lead to the same effects, that is, whether higher vapour rates could be used and less complex products obtained when the reaction is carried out under conditions of highly turbulent flow.

Materials

The experiments described below were carried out with two samples of gas-oil and one of kerosene obtained from Imperial Oil Ltd. These samples were marked respectively A, B, and C. The specific gravity, aniline point, and A.S.T.M. distillation data of each sample are given in Table I.

Experiments 396 and 398 were carried out with gas-oil A; Experiment 402 with sample C; all other experiments were carried out with sample B.

Apparatus

All experiments were carried out with a 28% chromium alloy reaction tube (Allegheny 55) having an internal diameter of 2.5 cm. and a heated length of 145 cm.

In Experiments 406 to 410 no baffles were used. All other experiments were carried out in a tube fitted with baffles consisting of circular discs, 2.25 cm. in diameter, cut from 0.37 mm. sheet, supported 1.6 cm. apart on a 0.65 cm. rod that extended

TABLE I

PROPERTIES OF CHARGING STOCKS USED

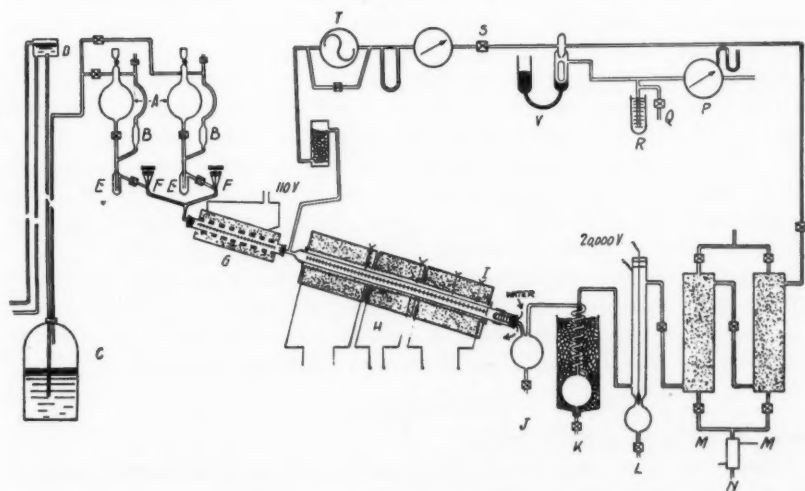| Sample	A	B	C
Sp. gr. at 25°C.	0.853	0.855	0.803
Aniline point	63.0	62.2	—
A.S.T.M. distillation, %	Temperature, °C.		
(1st drop)	213	215	189
10	232	233	205
20	239	240	209
30	245.5	245	213.5
40	253	251	217
50	263	260	223
60	274	270	228
70	289	284	233.5
80	308	300	241
90	338	337.5	252.5
End	373	—	272

FIG. 1. *Apparatus used in vapour-phase cracking of gas-oil.*

throughout the heated length of the tube. The baffles and support were of the same material as the tube.

A diagram of the apparatus is given in Fig. 1.

The furnace was heated by means of nichrome windings wound in sections and well insulated, the current supplied to each section being independently controlled. Temperatures were determined by means of thermocouples, I, placed in the air space between the winding and the tube, the distance between the winding and the tube wall being about 1 in.

The volume of the reaction space was 690 cc.; this includes the volume of the first 30 cm. section which was kept at a lower temperature and was used as a vaporizer and preheater.

The liquid feed was controlled as follows: About 800 gm. of oil was put in one of the reservoirs, A, the liquid being kept under the air pressure corresponding to a 7 ft. head of water between the constant level tank, D, and the bottle, C. (The other reservoir, A, was used for other experiments in which large quantities of liquid were put through the furnace, the arrangement shown permitting recharging without interrupting the experiment.) It was found that under these conditions the control of the liquid rate through the graduated needle valve, F, was independent of any slight variation in the back pressure from the furnace. The rate of flow could be checked in the course of an experiment by closing the valve under the reservoir, and determining the time required by the liquid to run past the graduations on the small calibrated bulb, B. The trap, E, was put in to catch any solid particles and prevent stoppage of the needle valve. The liquid was partly vaporized in the electrically heated tube, G. This consisted of a 2.0 cm. quartz tube, 38 cm. long, the heat being supplied by means of a well insulated winding. The maximum current that could be supplied to this tube was insufficient to vaporize the oil completely at the high liquid rates used, and the first 30 cm. section of the cracking furnace was kept at 650° C. to complete vaporization and preheat the vapours. The vapours and gases from the furnace were cooled by means of a water cooled copper spiral before emerging from the tube. Some of the vapours condensed in J and in the ice cooled condenser, K, and the tar-fog carried over was precipitated in the Cottrell, L, the condensable vapours being removed from the gas by the charcoal absorbers, M. The residual gas passed through the valve, V, and past the trap, R, and the meter, P, to waste, samples being taken at Q during each experiment.

In the last series of experiments a fraction of the off-gas was recirculated through the furnace by means of the pump, T, the valve S being opened. The amount of gas recirculated was controlled through the valve, V. The rest of the gas was allowed to escape through the meter, P, as before.

Experimental

Single Pass Cracking Experiments

A few preliminary experiments were made with gas-oil A and kerosene C, a baffled tube being used. The data given in Table II are typical of the

results obtained in these experiments. In the same table are given the results obtained in the experiments carried out under carefully controlled conditions, gas-oil *B* (Experiments 406 to 415) being used. The composition of the gases obtained in the above experiments is given in Table III.

TABLE II

GASOLINE YIELDS IN BAFFLED AND UNBAFFLED TUBES

No.	Oil sample	+ or − baffles	Oil charged		Temperature, °C.		Liquid products,		205° end-point gasoline	
			Total	Rate, gm./hr.	1st section	2nd section	Total, gm.	Per cent yield, based on oil put through	Per cent of total liquid	Per cent yield, based on oil put through
396	A	+	819.0	2240	535	645	458	56.0	37	20.7
398	A	+	750.5	2145	565	710	367.7	49.0	47	23.0
402	C	+	716.3	2390	630	782	265.0	37.0	60	22.2
406	B	−	763.8	2035	595	600	678.0	88.8	9.5	8.4
407	B	−	765.5	2090	585	650	649.0	84.8	19	16.1
408	B	−	762.0	2080	520	700	559.6	73.5	26	19.1
409	B	−	748.0	2090	595	750	463.5	62.0	36	22.3
410	B	−	759.5	2068	670	800	403.0	52.9	45	23.9
411	B	+	755.1	2210	550	600	636.4	84.3	19	16.0
412	B	+	755.8	2110	590	650	544.9	72.1	31	22.4
413	B	+	752.8	2100	610	700	408.0	54.2	45	24.4
414	B	+	768.2	2142	600	750	336.0	43.7*	46	20.1*
415	B	+	816.5	2225	630	800	363.6	44.5	50	22.3

* *Some of the liquid from the charcoal absorbers was lost.*

TABLE III

COMPOSITION OF GASEOUS PRODUCTS

No.	Total gas, litres	Litres/ hr.	Composition (% by volume)							Total olefines produced, gm.		Per cent yield olefines, based on oil put through
			C_2H_2	C_2H_4	C_3H_6	C_4H_8	H_2	Residue		C_2H_4	C_3H_6	
								%	C_n*			
396	89.7	245	0.0	35.1	2.1	0.0	10.4	52.4	1.14	–	–	–
398	264.5	757	2.6	20.9	25.3	3.3	10.5	37.4	1.00	69.1	125.5	25.9
402	314.6	1050	1.3	28.0	18.4	1.0	12.4	38.9	1.07	110.1	108.5	30.5
406	34.1	91	0.1	20.8	20.9	1.7	7.7	43.4	1.27	8.9	13.4	2.9
407	72.3	197	0.3	21.4	25.2	0.9	9.3	40.9	1.22	19.3	34.2	7.0
408	132.0	361	0.5	19.8	27.1	3.8	9.7	37.5	1.08	32.7	67.0	13.1
409	205.0	560	0.4	21.5	24.6	2.8	11.5	38.1	1.12	55.1	94.5	20.0
410	283.0	770	0.6	22.4	22.8	0.4	12.9	39.9	1.06	79.2	121.0	26.3
411	69.1	173	0.0	18.3	29.9	2.8	8.2	39.6	1.21	15.8	38.7	7.2
412	124.3	347	0.6	19.2	28.8	4.2	9.2	37.7	1.23	29.8	67.1	12.8
413	233.0	650	0.6	20.4	26.6	3.2	9.8	38.6	1.09	59.4	116.4	23.4
414	325.8	908	1.0	21.7	19.8	5.8	11.8	39.0	1.08	88.4	121.0	27.2
415	370.0	1010	0.5	24.4	12.6	1.1	16.5	44.4	1.01	112.8	87.4	24.5

* *Carbon number of residue.*

The results of the preliminary experiments, Nos. 396, 398, 402, showed that the optimum temperature for the vapour-phase cracking of the petroleum fractions used was below 800° at rates of about 2000 gm. per hour. As this was well within the temperature range at which the furnace could be operated and as the liquid recovery apparatus was found adequate for collecting the liquids in the off-gas, the above rate was adopted in subsequent experiments.

As already stated, the conditions under which Experiments 406 to 415 were carried out were carefully controlled in order to determine the effect of induced turbulence, particularly on the amount of cracking at a given temperature, and on the nature of the liquids produced. In the first five of the above-mentioned experiments no baffles were used; in the last five, baffles were used.
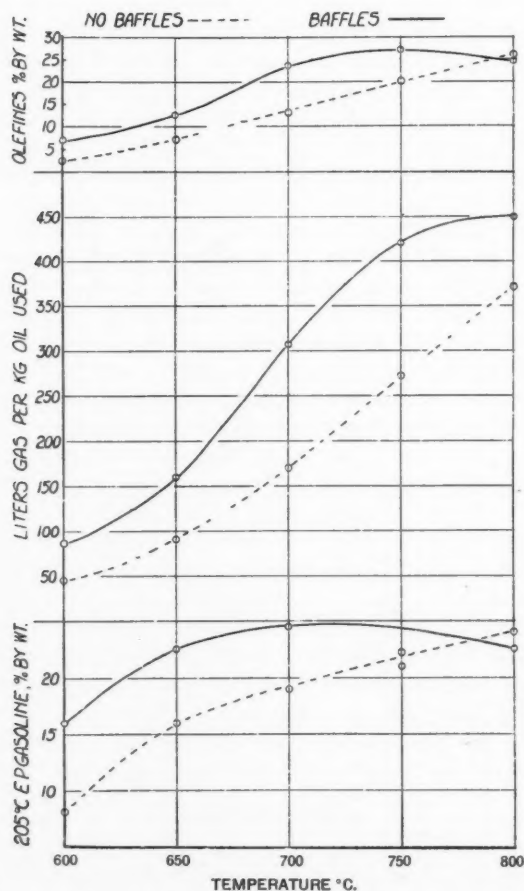

FIG. 2.   *Effect of baffles on yield of gasoline and gaseous products.*

Yield of 205° C. End-point Gasoline

The yields of 205° end-point gasoline obtained on one passage in the baffled and in the unbaffled tube respectively have been plotted in Fig. 2. Curves showing the amounts of gas produced and the yields of olefines under the two conditions have been plotted in the same figure. It will be observed that under otherwise identical conditions as to temperature and gas-oil rate, the amount of cracking, as shown by the yield of low boiling products and of olefines, is almost double in the temperature range 600 to 700° when baffles are used. It will also be observed that the yield of 205° end-point gasoline is about the same at 650° C. in the baffled tube as at 750° C. in the open tube. The difference in the amount of cracking under the two conditions is obviously due to the considerably higher rate of heat transfer from tube wall to vapour in the baffled tube, in spite of the fact that the vapour velocity in the open reaction tube was undoubtedly in the critical range at which turbulence appears. The foregoing results confirm the data previously obtained in experiments on the pyrolysis of hydrocarbon gases (1, 2, 3, 4). In fact, the efficiency of the particular design of baffles used in producing a high degree of turbulence, and consequently a high rate of heat transfer, appears to be markedly greater in the case of the heavy petroleum vapours than with hydrocarbon gases.

It is interesting to compare the results obtained at 800° C. by the use of a baffled tube with the results obtained by Groll (8) at the same temperature by the use of an open tube. In Experiments 1 to 10 (8, p. 790), for instance, Groll obtained a conversion of gas-oil to 205° end-point gasoline of 18.5% at 800° C. The composition of this gasoline, as shown by its distillation curve, is very similar to that of the low boiling products obtained at the same temperature in our Experiment 427 in a baffled tube, but the yield of gasoline in the latter experiment was 22.3% of the gas-oil charged. The striking difference between the two experiments, however, lies in the rates of throughput under the two conditions. In Groll's experiment, the gas-oil was put through at the rate of 1.32 litres per litre of reaction space per hr., while in our experiments the corresponding rate was 3.77 litres per litre per hr., an increase of almost 200%. Although the observed temperature was the same in both cases, it may be pointed out that the temperature in Groll's experiments was recorded by means of a thermocouple placed along the axis of the reaction tube, while in our experiments, in which electrical heating was used, the thermocouples were placed in the air space between the heating elements and reaction tube. Hence it is probable that the temperature recorded under our conditions was appreciably higher than that which would have been recorded by thermocouples placed inside the reaction tube.

In Groll's experiment it was found necessary to introduce a small amount of steam along with the oil vapours, in order to suppress carbon formation. We found the addition of steam unnecessary, the deposition of carbon being negligible in the experiments with baffles, this being due in part to the high vapour rates used, but mostly to the more even temperature distribution throughout the reaction chamber and the decrease in the thickness of the stationary gas film on the heating surface resulting from turbulence.

Composition of the 205° C. End-point Gasoline

The use of baffled cracking tubes was found to have a very pronounced effect on the composition of the low-boiling liquids produced at temperatures above 650° C.   A comparison of the distillation curves obtained on fractionating the liquids in experiments in baffled and in open tubes shows that the amounts of aromatics present in these liquids at the higher temperatures are very much greater when baffléd tubes are used.   These curves have been plotted in Fig. 3.   It will be seen, for instance, that the percentage of benzene and toluene in the experiment at 800° in the baffled tube amounts to about
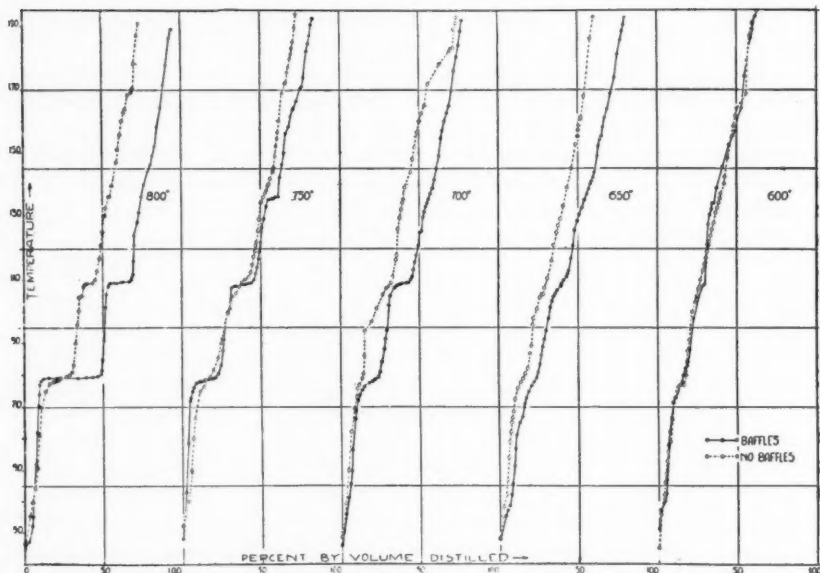

FIG. 3.   *Fractional distillation curves for light oils obtained at various temperatures in straight run experiments in open and in baffled tubes.*

60% of the 205° end-point gasoline, whilst an experiment under the same conditions in the open tube yielded a product containing less than 30% of these two aromatics.   It is interesting to note that the fractionation of the liquids obtained in the baffled tube at 750° gave quite a sharp xylene cut, which, however, contained some styrene.   Bromination of the xylene fractions indicates that, although styrene is always present in appreciable amounts in the liquids produced at 800°, the xylenes virtually disappear, being apparently broken down to simpler aromatics.   This breakdown of alkylated aromatics into unsubstituted ring compounds at higher temperatures has been observed by Groll (8, p. 793).

The liquids produced at low temperatures consist predominantly of the primary decomposition products of the heavy paraffins, and therefore consist

of a mixture of olefinic and paraffinic fragments.   The complexity of the low-boiling liquids produced under these conditions is well shown by the distillation curves of the products obtained at 600° and 650° C., and also by their high iodine numbers.

The distillation curve of the product obtained at 700° C. in the baffled cube indicates that an appreciable fraction of the olefines first produced have polymerized to form aromatics, whilst at the same temperature, in the open tube, the low boiling products are still highly complex.   Similarly at 750° and 800° C., increasing amounts of olefines are converted to aromatics in the baffled tube, whilst in the open tube the formation of benzene and toluene only becomes appreciable at 800° C.

The iodine numbers of the 205° end-point gasoline obtained in the above-described experiments—and the iodine numbers of the benzene and toluene fractions—have been plotted in Fig. 4.   It will be observed that the 205°
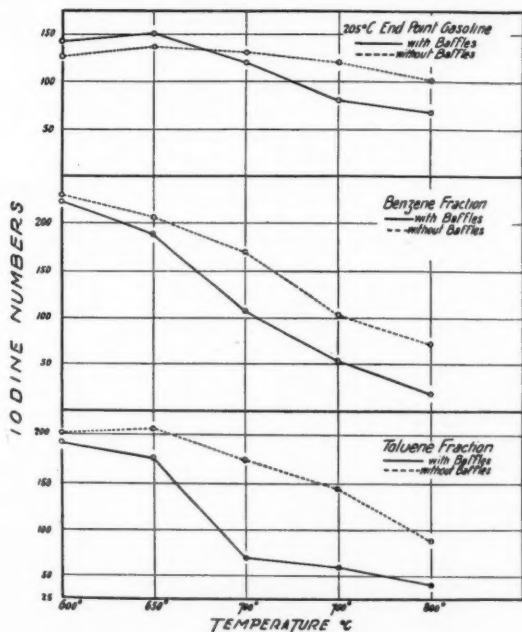

FIG. 4.   Iodine numbers of light aromatic fractions.

end-point gasoline produced at 600° and 650° with baffles contains more olefines than that produced at the same temperature in the open tube.   The corresponding benzene and toluene fractions, however, contain less unsaturateds, and consequently the higher iodine number referred to above is probably due to the presence of amylenes and hexenes which have escaped further decomposition.   It is interesting to note the very marked difference in the

iodine numbers of the benzene and toluene fractions of the liquids produced at 750° and 800° C. with and without baffles. This result was of course to be expected from the sharply defined benzene and toluene plateaus in the distillation curves of the liquids produced in the baffled tube, as compared to the curves obtained on distilling the liquids obtained with the open tube. As already mentioned, the main difficulty that has rendered impractical the production of aromatics by the vapour-phase cracking of petroleum is the complexity of the products obtained. It would appear, however, that the isolation of aromatics from the liquids produced by the vapour-phase cracking of petroleum in baffled tubes would be a comparatively simple operation, and further, in view of the high yields obtained, heavy petroleum fractions may be regarded as a potential source of aromatics by that process.

Composition of the Heavy Residues

The heavy residues, that is, those fractions of the liquid products boiling above 205°, were subjected to an A.S.T.M. distillation. The figures are given in Table IV.

TABLE IV

A.S.T.M. DISTILLATION OF HEAVY RESIDUES

Experiments without baffles

Experiment Temperature, °C.	406 600	407 650	408 700	409 750	410 800
1st drop, °C.	212.5	210	209	207	212
10% over	231.5	232	231	231	234
20	234	238	238	240	244
30	244	245	245	248	256
40	251	251	251	258	268
50	259	259	262	270	285
60	271	271	275	285	303
70	287	287	293	305	327
80	307	308	314	327	331 (74%)
	338 (90%)	339 (90%)	345 (90%)	335 (87%)	
Density (20° C.)	0.862	0.867	0.881	0.906	0.942

Experiments with baffles

Experiment Temperature, °C.	411 600	412 650	413 700	414 750	415 800
1st drop, °C.	212	213	206	212	Quantity of
10% over	231	232	232	240	residue in-
20	238	240	242	251	sufficient for
30	244	247	252	265	distillation.
40	252	255	262	286	
50	260	262	272	306	
60	270	276	292	323	
70	284	291	315	330	
80	306	311	333	334 (72%)	
	338 (90%)	345 (90%)	338 (85%)		
Density (20° C.)	0.869	0.891	0.942	0.992	

The boiling range and densities of these fractions show that the heavy residues obtained below 700° C. without baffles and below 650° C. with baffles contain a large proportion of unchanged paraffins. In Experiment 412, for instance, in which the yield of gasoline was 22.4% on one passage, the heavy residue represented 50% of the oil put through, and from the distillation range of this material and its specific gravity one would expect an appreciable increase in the yield of gasoline on recycling. It would appear that the optimum temperature under the conditions studied would be between 600 and 650° C., with recycling, if maximum production of aromatics is not desired. The specific gravity of the fractions obtained at temperatures higher than 750° C. indicates the presence of increasing amounts of aromatics. The composition of these fractions was not investigated any further, and the amounts obtained were insufficient to permit the carrying out of recycling experiments.

Recirculation Experiments

A series of experiments was carried out to determine the effect of recirculating a fraction of the off-gas with the oil vapours through the cracking furnace. This was done in an attempt to improve the vapour flow conditions in the cracking tube, and to increase, if possible, the yield of aromatics by polymerizing some of the olefines present in the off-gas. A baffled tube was used in all experiments.

The results obtained are recorded in Tables V and VI.

TABLE V

YIELD OF 205° END-POINT GASOLINE IN RECIRCULATION EXPERIMENTS

No.	Oil put through		Off-gas	Temperature, °C.		Liquid products		205° End-point gasoline	
	Total, gm.	Rate, gm./hr.	Recycling rate, litres/hr.	1st section	2nd section	Total, gm.	Per cent yield based on oil put through	Per cent of total liquid	Per cent yield based on oil put through
428	724	1057	251	650	800	342.6	47.3	47.0	22 2
429	741	1060	224	650	750	355.7	47.9	47.7	22.9
430	73ſ	1060	220	650	700	370.0	50.7	41.7	21.1
431	680	1360	216	655	800	317.8	46.7	45.3	21.2
432	750	2050	248	660	800	346.6	46.2	46.1	21.3
433	750	2140	245	680	750	406.5	54.1	38.7	21.0
434	750	2140	221	660	700	496.7	66.1	30.8	20.4

It will be observed that recirculation did not improve the yield of 205° end-point gasoline based on oil put through, even at low liquid rates, and resulted in an appreciable decrease in the percentage of benzene and toluene in the low boiling products obtained at 750° and 800° C. The latter result was unexpected, as it was believed that the formation of aromatics would be favoured by increasing the time of contact of the gases containing a high

TABLE VI

COMPOSITION OF GASES OBTAINED IN RECIRCULATION EXPERIMENTS

No.	Gas produced		Composition						Total olefines produced, gm.		Per cent yield olefines based on oil put through
	Litres /hr.	Total gas, litres	C_2H_2	C_2H_4	C_3H_6	H_2	Residue		C_2H_4, gm.	C_3H_6, gm.	
							%	C_n			
428	468	316	1.0	22.7	10.6	15.7	50.0	1.0	89.7	63.0	21.5
429	450	315	0.8	17.6	18.2	13.8	49.6	1.0	69.3	107.8	23.9
430	331	228	1.0	20.4	14.1	–	–	–	–	–	–
431	627	314	1.0	22.9	10.9	14.2	51.0	1.0	89.8	64.3	21.1
432	895	328	1.2	19.7	20.9	9.7	49.1	1.0	80.7	129.0	30.8
433	617	216	1.3	20.7	26.8	10.4	50.8	1.06	55.9	109.0	22.0
434	376	132	1.3	18.6	28.7	9.2	42.2	1.05	30.6	71.1	13.6

concentration of olefines. The distillation curves of the products obtained in the above-mentioned experiments, Fig. 5, also show that the low boiling fractions, in particular those obtained at 750° and 800° C., are more complex than
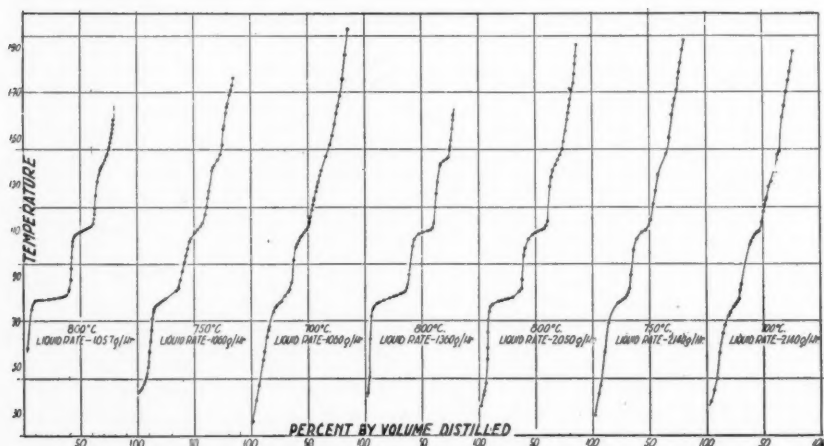

FIG. 5. Fractional distillation curves for light oils obtained at various temperatures in recycle experiments in baffled tubes.

the corresponding fractions from single pass cracking experiments. On the other hand, the A.S.T.M. distillation data and specific gravity of the heavy residues, that is, of that fraction of the liquid products boiling above 205° C., show that the heavy residues from experiments carried out with recirculation contain less aromatics or other condensed products than the corresponding fractions from single pass cracking experiments, and consequently would probably give higher yields of gasoline on recycling.

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THE INFLUENCE OF TEMPERATURE ON THE SORPTION OF SODIUM HYDROXIDE ON WOOD[1]

By G. R. Lusby[2] and O. Maass[3]

Abstract

The sorption of sodium hydroxide on black spruce has been measured at 20°, 50°, and 75° C., and was found not to change very much between 20° and 75°. An increase in temperature causes the break in the sorption curve to occur at a higher concentration of alkali. Cooking action begins between 50° and 75°, and tends to obscure the effect of an increase in temperature above 50°.

Introduction

In the alkali-cooking of wood, sorption must play a part, and for the interpretation of the mechanism of cooking, data regarding the influence of temperature and concentration changes on the amount of sorption must be made available. Richardson and Maass (10) made measurements of the sorption of sodium hydroxide on white spruce wood at room temperature. In the present work it was considered of interest to carry out similar measurements on a different species of wood, and to attempt to measure the sorption existing at temperatures approaching the range in which cooking takes place. Since the sorption data are to be used for elucidating the mechanism of cooking, the mechanism of sorption itself should be determined first.

Cotton has been used as the source of cellulose in virtually all researches on alkali sorption recorded in the literature, little work having been done on wood. For reviews of the extensive literature relating to alkali sorption the reader is referred to papers by Clibbens (3), Blanco (2), and Schwarzkopf (12).

When any form of cellulose is placed in a solution of sodium hydroxide, the concentration of the latter decreases rapidly and reaches a constant value within a short time. The explanation of this phenomenon is that sodium hydroxide has been taken up by the cellulose. Since cellulose has a strong affinity for water, it is certain that water also must be taken up by the cellulose in the alkaline solution. The observed decrease in concentration then represents the net effect of the sorption of sodium hydroxide and water by the cellulose. For this reason Neale (7, 8, 9) describes this phenomenon as a "preferential absorption" of sodium hydroxide. Richardson and Maass (10) use the term "pseudo sorption" with the same meaning, since in the calculation of the alkali taken up by the cellulose, the water taken up is neglected. The extent to which this value differs from the true quantity of sodium hydroxide taken up by cellulose depends to a large extent on the amount of water taken

up.   The simple general term "sorption" will be used in this discussion with the meaning of "alkali preferentially taken up" by wood or cellulose.

Vieweg (13) found that when the amount of sodium hydroxide sorbed by cotton is plotted against concentration of alkali, a sharp rise in the curve is noted at a concentration of 3 to 4 molar.   The curve then flattens out and becomes horizontal.   At a concentration of about 9 molar, another rise, or "break", in the curve occurs.   Vieweg (14) repeated this work in 1924 and obtained a slightly different curve.   Other workers have obtained similar results.   In Fig. 1 the dotted line represents data obtained by Heuser and Bartunek (5).   Rumbold (11) obtained a sorption curve with a flat part in the concentration range 1.0 to 1.9 molar.   Richardson and Maass (10), as a result of accurate sorption measurements at high concentrations of sodium hydroxide, showed that there is another flat part in the sorption curve besides the parts observed by Vieweg, Rumbold and others.   A curve indicating flat parts was also found in the case of white spruce by Richardson and Maass (10), and the breaks in both curves, *i.e.*, for cellulose and for wood, occurred at the same concentrations of alkali.

Few sorption measurements have been made at temperatures other than room temperature.   D'Ans and Jäger (4) determined the sorption of sodium hydroxide on pulp and cotton at 2° C., and Beadle and Stevens (1) obtained isothermals between 5° and 40°.   The results obtained by these writers show that an increase in temperature decreases the amount of sorption and increases the concentration at which the break in the curve occurs.
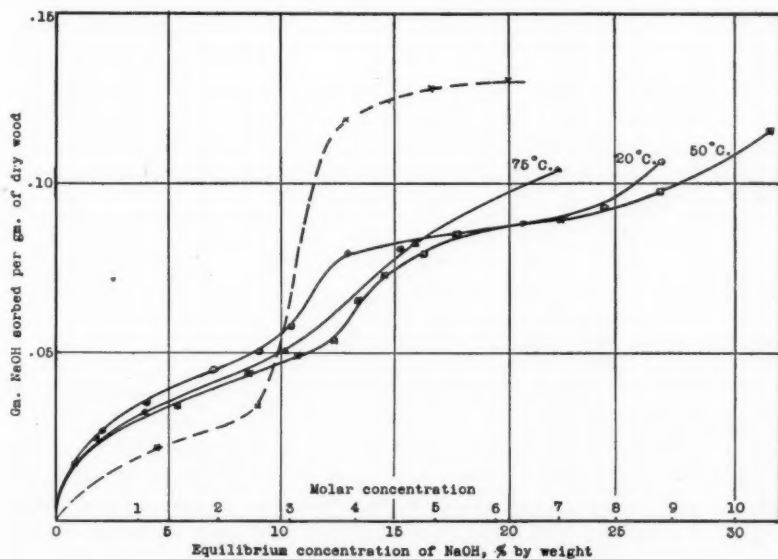

FIG. 1.   *Sorption of sodium hydroxide on black spruce in one hour.*

TABLE I

SORPTION OF SODIUM HYDROXIDE ON BLACK SPRUCE
AT 20° C.

Equilibrium concentration, molar	Sorption, gm. per gm. of wood	Equilibrium, concentration, molar	Sorption, gm. per gm. of wood
1.030	0.035	7.640	0.089
1.069	.036	7.790	.096
2.808	.058	8.690	.107
2.873	.058	8.750	.104
3.623	.080	11.25	.153
3.755	.079	11.51	.109
4.453	.078	11.53	.096
4.520	.080	13.03	.099
6.380	.088	13.28	.082
6.425	.085	—	—

TABLE II

SORPTION OF SODIUM HYDROXIDE ON BLACK SPRUCE
AT 50° C.

Equilibrium concentration, molar	Sorption, gm. per gm. of wood	Equilibrium concentration, molar	Sorption, gm. per gm. of wood
0.2308	0.0172	3.735	0.043
0.2345	.0193	3.803	.063
0.2448	.0186	3.820	.068
0.2510	.0170	4.075	.073
0.4918	.0202	4.083	.072
0.4975	.0244	4.768	.076
0.5020	.0247	4.820	.081
0.5113	.0142	5.260	.093
0.5120	.0252	5.306	.075
1.133	.0335	5.315	.080
1.440	.0339	5.321	.090
1.445	.0340	6.965	.090
2.315	.0430	7.010	.089
2.325	.0376	8.655	.096
2.943	.048	8.655	.098
3.000	.051	10.60	.122
3.483	.054	10.61	.117
3.500	.053	14.70	.159
3.653	.059	14.90	.112
3.685	.048	14.93	.140
3.703	.056	—	—

TABLE III

SORPTION OF SODIUM HYDROXIDE ON BLACK SPRUCE
AT 75° C.

Equilibrium concentration, molar	Sorption, gm. per gm. of wood	Equilibrium concentration, molar	Sorption, gm. per gm. of wood
1.047	0.0320	6.925	0.103
1.093	.0342	6.975	.105
2.783	.049	9.010	.129
2.900	.051	9.145	.085
4.650	.082	12.09	.135
4.683	.082	12.13	.108

Experimental Procedure

For details of experimental procedure, the reader is referred to the paper by Richardson and Maass (10), who made determinations at room temperature; in the present work, measurements have been made at temperatures as high as 75° C. Slight modifications were introduced to eliminate errors brought about by the higher vapour pressure of water at 75°. The accuracy was similar to that obtained by Richardson and Maass. Instead of white spruce, black spruce was used, and the samples were prepared in the manner described by Richardson and Maass. The weight of sample used in an experiment varied from 1.8 to 3.8 gm. and the volume of solution was 8 to 10 ml. per gm. of wood. All calculations were based on the oven-dry weight of wood.

Experimental Results

The data obtained are given in Tables I, II, and III, and are presented in the form of isothermals in Fig. 1.

Discussion

The 20° isothermal is quite similar to that obtained by Richardson and Maass (10) for white spruce. The 50° isothermal shows that the effect of an increase in temperature is to cause the break in the curve

to occur at a higher concentration of alkali. It would be expected that the break in the 75° isothermal should lie to the right of that in the 50° isothermal, but actually most of the sorption values at 75° are intermediate between the 20° and 50° values.

The high sorption values at 75° appear to be due to the cooking action which takes place at that temperature. This was indicated by the results of experiments in which wood was placed in sodium hydroxide solution and the concentration determined at various times. At 20° the change in concentration was found to be complete within one hour. At 50° there was a small change after one hour, and at 75° a considerable change. The rate of change in concentration at 75° gradually decreased, but was such that at the end of two days the calculated "sorption" value was almost double that at the end of one hour. The probable explanation of the change after one hour is that cooking action liberates acids of such strength that after they combine with the alkali the latter cannot be titrated with hydrochloric acid with methyl orange as indicator. With cooking action taking place at 75° no precise evaluation can be made of the change caused by raising the temperature from 50° to 75°. It may be concluded, however, that the values of the sorption of sodium hydroxide on black spruce are not very much affected by raising the temperature.

The results confirm the work of Richardson and Maass in regard to the first break in their sorption curve for wood. The effect of temperature change on the position of this break in the curve is similar to that observed by Beadle and Stevens (1), and D'Ans and Jäger (4), who worked with pure cellulose.

Along the flat part of the curve, the sorption per gram of cellulose is considerably greater for wood (based on a content of 50% cellulose) than for cotton. The indication is that lignin and other wood substances, in addition to cellulose, take up alkali.

There has been a considerable amount of speculation concerning the interpretation of the curves showing sorption of alkalis on cellulose. Morrison, Campbell, and Maass (6) have found that the heat of sorption of sodium hydroxide on cellulose, when plotted against concentration of alkali, gives a curve having a break at the same concentration as that in the sorption curve.

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THE HEAT CONTENT OF WATER ADSORBED ON CELLULOSE[1]

By J. H. Shipley[2], W. Boyd Campbell[3], and O. Maass[4]

Abstract

The heat capacity of water adsorbed on cellulose has been measured by means of a new type of adiabatic calorimeter and a new experimental technique. Measurements have been made with 2, 4, 8, and 12% adsorbed water over the temperature range −35° to +25° C. with considerable accuracy. A mechanism, that of a change in the amount of bound water with the temperature, has been suggested to explain the high values obtained for the apparent specific heats of adsorbed water.

Introduction

From the results reported by the authors in a previous paper (7), and from further results obtained with mercerized cellulose, it seems apparent that there was an error inherent in the original procedure followed in those previous experiments involving measurements made at very low temperatures with cellulose containing adsorbed water. Since the cellulose containing the sorbed water was cooled down very rapidly when the container was plunged into the cold thermostat, it was thought that it would be possible for water to distil from the cellulose to the container wall if there was an appreciable temperature difference between the cellulose and the wall for any length of time. To investigate this possibility, one junction of a thermocouple was embedded in the cellulose and the other was fastened to the container wall, and the leads were connected through a variable resistance to a sensitive galvanometer. On immersion of the sample in the cold thermostat, the temperature differences between the cellulose and the wall were determined at definite time intervals. From tables of percentage relative vapour pressure in a cellulose-water system the allowable temperature difference, under which no distillation would occur, was calculated and found to be 4° C. The rate at which the sample could be cooled down and yet never give a temperature difference greater than 4° C. was found to be 2° C. per min.

Experiments were made to determine the values of the heat capacity of the sorbed water when the sample was initially cooled rapidly and when cooled slowly. There was a considerable difference between the values for a high percentage of adsorbed water, especially at the low temperatures. But it may be pointed out that the results for the heat capacity of dry cellulose and the heat capacity of sorbed water at the higher temperatures are not affected by this factor.

With these disadvantages in mind it was deemed advisable to design a new adiabatic calorimeter that would be suitable for the measurement of the heat capacity of small amounts of sorbed water at low temperatures.

Experimental

1. *Description of the Apparatus*

The calorimeter was of the adiabatic-electrical type. Radiation thermels were used to maintain adiabatic control, and it was possible to detect a difference of 0.0001° C. between the temperature of the inner and that of the outer portions of the calorimeter. For the proposed work it was necessary to reduce the losses due to thermal conductance to a minimum, and also to reduce the heat capacity of the calorimeter to a value such that the heat capacity of the sorbed water could be obtained with the desired accuracy. Losses due to thermal conductance were very low, as the only direct connections to the inner container were the three bakelite legs upon which the container stands and the two wires conducting the current to the heating coil.

The novel feature of this calorimeter was that there was no liquid bath around the inner container, the heating coil being wound directly around the copper container. This eliminates the errors due to evaporation of the calorimetric liquid, which is large in the older types of calorimeters. Also, the heat capacity of the apparatus is reduced to a much lower value.

The container, which is shown in section in Fig. 1, was made in the form of a cylinder of very thin copper, fitted with a cover which screwed on to a rubber gasket, *A*, thus making a vacuum-tight join. There was a small opening in the cover fitted with a screw cap, *B*, and a vacuum-tight join was obtained with a small lead disc *C*. This small opening was used to evacuate and dry the sample after the cover was screwed down, and was later used to introduce water into the sample.

The sample, consisting of a very pure form of bleached sulphite pulp of density 1.57, was cut into discs and packed into the container. Ten copper discs, *D*, of 5 mils thickness were placed uniformly throughout the pulp to aid in establishing thermal equilibrium. The cover was attached and two very thin coats of bakelite varnish diluted with amyl acetate were applied to the container. These were baked

FIG. 1. *Calorimeter vessel.*

on to ensure electrical insulation and still preserve good thermal contact. After the dry weight of the sulphite pulp had been determined by heating to 100° C., evacuating for 14 hr., cooling, and weighing, the resistance element of No. 30 enamelled copper wire was wound non-inductively over the entire container in such a way as to provide uniform heating throughout. The size of wire used was that obtained by calculation to give the required rate of heating. Two coats of bakelite varnish were applied to ensure insulation, and a close-fitting copper cylinder fashioned from 5 mil copper sheet was placed over the coil and container to aid in the attainment of thermal uniformity.
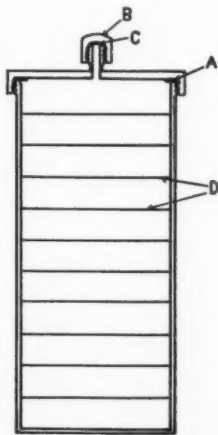
In its final form the container weighed 101.9364 gm., of which 26.6663 gm. was dried sulphite pulp. The calculated heat capacity per degree was 16.6 cal., of which half was contributed by the sulphite pulp. Actually the heat capacity per degree at about 25° C. was found to be about 16.9 cal. The resistance of the heating coil was 10.45 ohms at 23.0° C.

A diagrammatic section of the calorimeter is shown in Fig. 2. The outer jacket, A, was made of $\frac{1}{16}$ in. brass and was made vacuum tight by means of six bolts that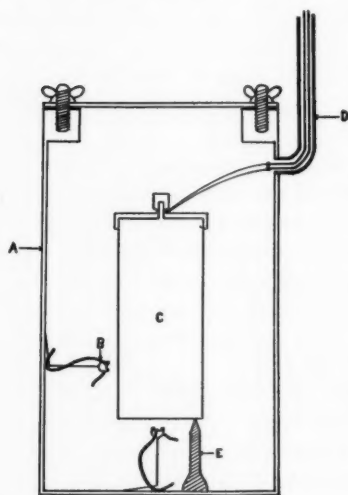 pressed the lid against a rubber gasket. The central portion was supported on three bakelite legs, E, which were cut to a point to minimize thermal conduction. In the space between A and C was mounted the radiation thermel, B, consisting of 13 pairs of junctions, 12 being arranged symmetrically around the sides and one on the bottom. One junction of each pair was supported at a distance of 2 mm. from C, and the other was in thermal contact with the jacket, A, being electrically insulated from it by a thin piece of mica.

FIG. 2.   *Adiabatic calorimeter.*

The size of the wire for making the connections to the resistance coil was of some importance, as the larger the size the greater the thermal conductance for a given temperature difference; on the other hand, if the wire were too fine an appreciable amount of heat would be developed in the connecting wire by the current. A calculation indicated that No. 26 copper wire was the optimum size. These leads were soldered to heavy copper connections that passed out of the apparatus through the brass side tubes, D. The leads to the radiation thermel passed through another side tube, the potential leads through a third tube, while a fourth tube was provided for evacuating and for filling the calorimeter jacket with dry air.

The whole assembly was immersed in a well insulated, large vacuum flask containing acetone. Acetone was used because, at low temperatures, water from the air would condense and form ice if it were not soluble in the liquid bath. The acetone was stirred by means of a current of dry air, and the temperature was measured with Beckmann thermometers. The bath was provided with electric heaters for raising the temperature, whereas for lowering the temperature small pieces of solid carbon dioxide were dropped in.

The electrical circuits are shown in a simplified form in Fig. 3. R is the calorimeter heater and R_1 a standardized resistance with a very low temperature coefficient of resistance. R_2 is approximately equal in resistance to R and is used to draw current prior to a run so as to bring the battery, B,

to as constant a voltage as possible. R_3 is a variable resistance by means of which the current through the system may be varied; it thus controls the rate at which the temperature rises.   The voltage leads to the potentiometer, P, are indicated by light lines.   The thermels are connected to the sensitive galvanometer, G, which has an optical path of about four metres to the scale.
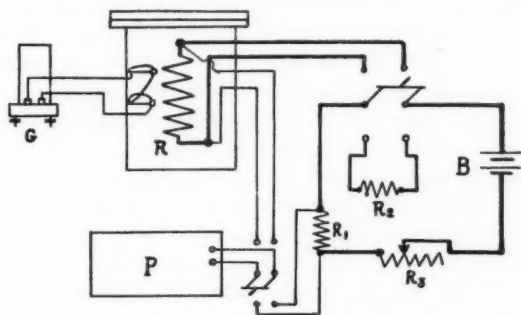

FIG. 3.   *Electric connections for adiabatic calorimeter*

By measuring the voltage drops across R and R_1 and the time interval during which the current is flowing, the heat input may be calculated from the relation

$$Q = \frac{E_1 \times E_2 \times t}{R_1 \times 4.185} \text{ cal.,}$$

where E_1 = potential drop across R_1 (volts),
    E_2 = potential drop across R (volts),
    R_1 = standard resistance (8.627 ohms),
    t = time in seconds.

2. *Standardization of Beckmann Thermometers*

Five Beckmann thermometers that were set for use at approximately $-35°$, $-20°$, $-5°$, $+5°$, and $+25°$ C. were employed in conjunction with this apparatus.   The zero point for each was determined by comparison with a calibrated platinum resistance thermometer.   In all the experiments the thermometers were used within $0.1°$ C. of the point at which they had been standardized, and therefore there was no necessity for calibrating them over the entire scale.

3. *Procedure*

The procedure adopted in making a determination of the heat capacity of the container plus contents is as follows.   The calorimeter bath was cooled to several degrees lower than the desired initial temperature so that the container and contents could be cooled by radiation and conduction in a reasonable time.   The resistance coil around the container proved of immense value as a resistance thermometer in the determination of the approximate

temperature of the container. This obviated the necessity of repeatedly bringing about thermal equilibrium by warming the outer bath to determine the temperature of the container. Also, the rate at which the container cooled down could be followed when the sample contained water, and thus any possibility of distillation of water from the cellulose to the cold wall could be guarded against. It was found that owing to the resistance of the air gap between the jacket and the container the maximum rate of cooling of the container was about 1°C. per min., which was well below that causing distillation.

When the container had cooled to the desired temperature the calorimeter was warmed to the required initial temperature by adjusting the temperature of the bath and by passing current through the heating coil. The exact initial temperature was determined by maintaining adiabatic conditions and reading the temperature of the outer bath by means of the suitable Beckmann thermometer. The current was then switched on and simultaneously the heaters in the outer bath were started. Adiabatic conditions were maintained by adjusting the current flowing through the bath heaters and also by the use of a spot heater and small pieces of solid carbon dioxide. In this way it was possible to keep the temperature difference between the bath and the inner vessel to about $\pm 0.004°$ C.

When the temperature had increased to that desired, the current was switched off and the exact time during which it was flowing was recorded. The final temperature was determined in the same manner as the initial temperature. During the course of the determination the voltages across the heating coil and the standard resistance were measured at intervals of 10 or 15 min., and the average values for E_1 and E_2 were employed in the calculations.

It was apparent that heat was conducted into the container along the current and potential leads, thus causing a definite rise in the temperature. This was partly overcome by immersing in the outer bath the first two feet of the current leads that projected from the side arm of the jacket.

The temperature rise appeared to the same extent in all the experiments, and therefore did not affect the results, as they were obtained by the difference between two series of runs. The same rate of heating was used at all times, so that the rise in temperature due to this leakage would be the same in all cases.

4. *Introduction of Water to the Sulphite Pulp*

After the total heat capacity of the container plus dry sulphite pulp had been determined, all the electrical connections were broken at the solder joints and the calorimeter was removed from the acetone bath. The container was taken out of the outer jacket, the leads to the coil being separated at the solder joins between the No. 26 connecting wires and the coil proper. The container was then weighed; the difference between this weight and the original was very small, and was due to the solder left on the current leads. The small cap was unscrewed, and redistilled water was introduced in approxi-

mately the required proportion by means of a small capillary tube. The cap was replaced and the exact amount of water introduced was determined by weighing.

To ensure an even distribution of the water throughout the pulp, the container was placed in an oven at 50° C. for 10 hr. It was then removed and allowed to stand at room temperature. This was repeated several times, and finally the container was replaced in the calorimeter jacket and the apparatus was reassembled.

5. *Experimental Errors*

For the measurement of time an accurate, calibrated chronometer or a stopwatch calibrated against this chronometer was used. The time interval of an experiment could be measured to 1 part in 20,000. The combined error in e.m.f. measurements was 3 parts in 10,000. The initial and final temperatures could be obtained to within $\pm 0.003°$ C., and therefore the probable error would be 1 part in 20,000. Over a 60° temperature interval ($-35°$ C. to $+25°$ C.) the probable experimental error is 0.04% in the heat capacity of the container plus contents. This corresponds to an error of about 0.08% in the heat capacity of the dry sulphite pulp.

Therefore the probable error to be expected in the heat capacity of the sorbed water will be 2.5% error for the water sorbed to the extent of 2%, 1.3% error for 4% sorbed water, and 0.7% error for 8% sorbed water.

From the results obtained with dry sulphite pulp over the temperature range $-35°$ to $+25°$ C. it was found that the heat capacity per degree for three successive experiments was 15.719, 15.722, and 15.731 cal. The average value was 15.724 cal. per degree and the mean deviation was ± 0.003 cal. This indicated that the error in this average value was 0.02%, which is in very good agreement with the value calculated above, as one would expect the actual error to be less than the calculated probable error.

Results

The total heat capacities of dry bleached sulphite pulp, and of 2, 4, 8, and 12% of adsorbed water were determined over the four ranges of temperature $-35°$ to $+25°$ C., $-20°$ to $+25°$ C., $-5°$ to $+25°$ C., and $+5°$ to $+25°$ C.

In Table I are summarized the mean values of the total heats of the container and contents between the initial temperatures given in Column 1 and the

TABLE I

TOTAL HEATS GIVEN UP BY THE CALORIMETER

(Cal., corrected to a final temperature $+ 25.00°$ C.)

Initial temp., °C.	Sulphite pulp	Sulphite pulp plus			
		2.0% water	4.0% water	8.0% water	12.0% water
−35.00	944.28	974.67	1002.47	1066.53	1135.01
−20.00	721.74	744.23	766.29	815.38	896.67
− 5.00	489.69	506.33	521.79	555.21	592.75
+ 5.00	330.13†	342.08	353.09	376.30	400.74

† *Calculated value.*

final temperature. Each value reported below is the mean of at least two determinations which agreed to 1 part (or less) in 1000.

The value of the total heat from $+5.00°$ to $+25.00°$ C. for the container plus dry sulphite pulp was determined from the following equation

$$H = 2667.3 + 1.9413T - 0.046548\ T^2 + 0.000033614\ T^2.$$

This equation represents the variation of the total heat content of container plus dry sulphite pulp with the temperature over the range $-35°$ to $+25°$ C. The value obtained by substituting for the temperature in the above equation is good to 1 part in 10,000, as indicated by the agreement between the other points which were determined both experimentally and from the equation.

The heat contents of the sorbed water, per gram of water, are given in Table II. The heat content of "2.0%" water (Column 2, Table II) was obtained by subtracting the values in Column 2 from those in Column 3 of Table I, that is, subtracting the heat content of the container plus dry sulphite pulp from the heat content of the container plus sulphite pulp plus 2.0% of water, and recalculating on the basis of 1 gm. of sorbed water. Similarly the heat contents of the other quantities of adsorbed water per gram of water were determined by subtracting the appropriate values and recalculating on the basis of 1 gm. of sorbed water.

TABLE II

TOTAL HEATS PER GRAM OF SORBED WATER

(Cal., corrected to final temperature $+ 25.00°$ C.)

Initial temp., °C.	2% water	4% water	8% water	12% water	4%–2% water	8%–2% water	8%–4% water	12%–8% water
−35.00	57.24	54.72	57.32	59.95	52.21	57.34	59.90	65.30
−20.00	41.40	41.90	43.91	46.50	41.44	44.42	45.90	51.77
− 5.00	30.63	30.19	30.72	32.39	29.05	30.52	31.25	35.80
+ 5.00	22.51	21.59	21.65	22.19	20.67	21.36	21.70	23.31

Discussion of Results

Bleached sulphite pulp was used because it could be obtained in a very compact form, and therefore a large amount could be packed into the container. Also, relative vapour pressure measurements showed that bleached sulphite pulp holds more water by surface adsorption than mercerized or standard cellulose. This would mean that any difference in heat capacity of the first portion of adsorbed water from that of the water subsequently added would be enhanced.

The heat capacities of 2, 4, 8, and 12% adsorbed water on bleached sulphite pulp (Table II) are shown graphically in Fig. 4. The surprising fact that there is no great difference between the heat capacities of the 2, 4, 8, and 12% adsorbed water is readily apparent from Fig. 4. This result was totally unexpected and is absolutely contradictory to previous conclusions made in

this laboratory and elsewhere which were based on experiments other than specific heat measurements.

Previous experiments (7) indicated that initially the water adsorbed is very tightly bound and may even be in the form of a surface compound with the cellulose. As water is subsequently added, the bonding becomes less secure and at approximately 8% sorption the water is probably condensing in the capillaries.
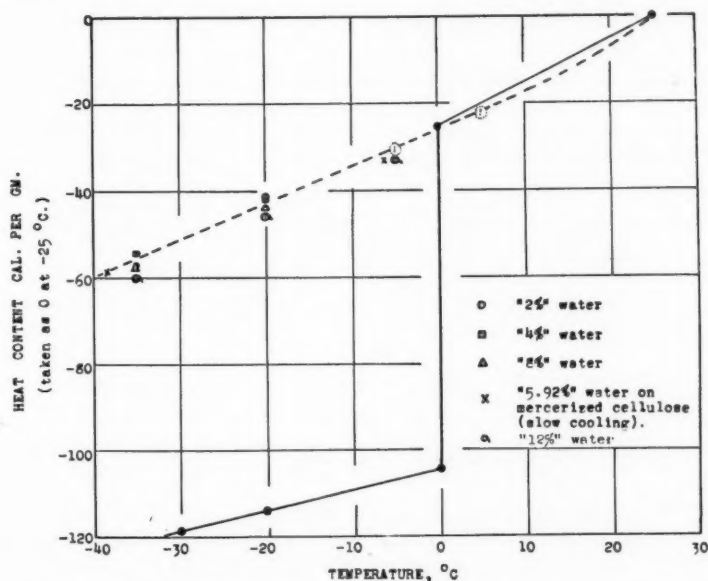

FIG. 4. *Heat content of adsorbed water between +25° C. and lower temperatures.*

It may be seen from Fig. 4 that the heat contents of 2, 4, 8, and 12% adsorbed water lie on curves that actually indicate a higher heat content for adsorbed water above zero degrees than the heat content of free water, which is indicated by the solid line. This is most unexpected since previous experiments on dielectric constant (2), heat of adsorption (1), vapour pressure (3, 8), and density (4) indicate that the first portions of adsorbed water are tightly bound. But such water must be partly restricted in movement, and therefore the number of degrees of freedom would be diminished. This would entail a lowering of the heat capacity. But the heat capacity is not lowered. Also, since with increase in water content the proportion of free water must increase, it would be expected that specific heat of the adsorbed water would increase markedly with rise in the quantity of water adsorbed. This also is not the case.

It seems reasonable to suppose that on cooling below 0° C. the adsorbed water will remain adsorbed and will not form ice, so that no latent heats of

fusion are to be expected. With increased water content and the existence of free water one would expect a possible heat adsorption due to freezing, although here also it probably would not occur owing to the phenomenon of supercooling when water exists in a state of very fine subdivision (6).
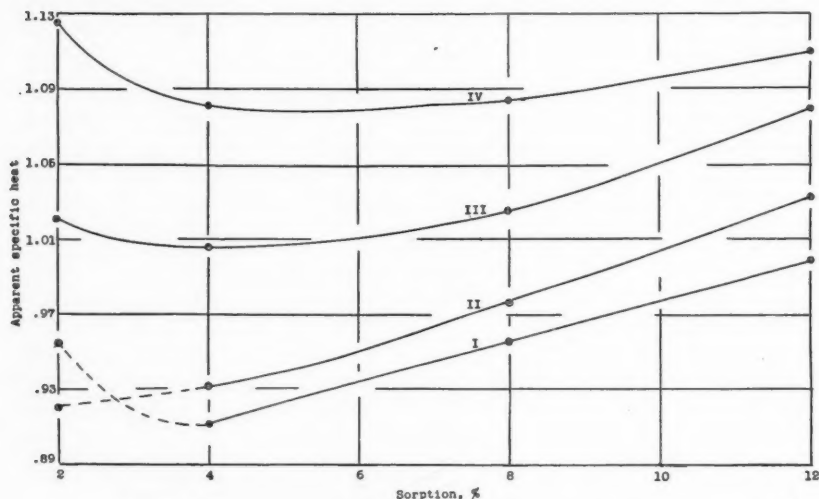

FIG. 5. *Variation of apparent specific heat of adsorbed water with percentage adsorbed.
I, −35° to +25° C.   II, −20° to +25° C.   III, −5° to +25° C.   IV, + 5° to +25° C.*

In Fig. 5 the average specific heats of the adsorbed water for the respective temperature ranges are plotted against the percentage of water adsorbed. Curve I is the average specific heat over the range of temperature −35° to +25° C., Curve II for the range −20° to +25° C., Curve III for the range −5° C. to +25° C., Curve IV for the range +5° to +25° C. It will be noticed that the specific heats are plotted on a large scale, so that any experimental error is greatly magnified. Nevertheless all the curves show a marked uniformity except that the values for 2% adsorbed water in Curves I and II seem to be interchanged. It is possible that this is due to experimental error.

The apparent specific heat over the temperature range +5° to +25° C. (Curve IV) is definitely above the specific heat of free water for all values of water content. The same may be said for the range −5° to +25° C., and those at the lower temperatures are not much below the specific heat of free water. The explanation that the high value may be due to the latent heat of fusion has already been ruled out in the previous discussion. Also, it may be seen that the high values for the specific heats are obtained for the range +5° to +25° C., and over this range the temperature has never been brought below the freezing point of water.

As the 2% adsorbed water, most of which must be bound, at least more so than in the higher quantities, gives the highest value for the specific heat at

+5° C., some source of heat absorption must be looked for other than that required for heating up the cellulose and water alone. It is suggested that some change in equilibrium in the system water-cellulose must occur which brings about an absorption of heat when the system is warmed up. Such a mechanism is corroborated by other facts, and it may be of considerable theoretical importance that attention has been drawn to the possibility of this mechanism.

The amount of water that is held by cellulose at any one concentration exists in various degrees of freedom, the term being used in the sense of the extent to which it is bound to the cellulose. It is suggested that a rise in temperature decreases the amount of bound water and increases the freedom of some water to the corresponding extent. The large heat of adsorption that was found by Argue and Maass (1) shows that the change from bound water to free water requires a large amount of heat. In the heat capacity measurements, the heat that was added was therefore required for two purposes, first, the heat capacity of the system as a whole, and second, to supply the heat necessary to bring about a decrease in the amount of bound water with rise in temperature. If this quantity were known and sub-tracted, the resultant specific heats of the adsorbed water would be less, and probably conform with what could be predicted from the other physico-chemical measurements.

Additional evidence that with rise in temperature the extent to which water is bound at a definite concentration decreases is given by the following con-siderations. It has been found by Urquhart and Williams (9) and by Walker (10) that, except at temperatures above those used in this work, if the relative humidity is kept constant and the temperature is raised, the amount of adsorbed water decreases, or that for a constant amount of adsorbed water the relative humidity has to be increased with rise in temperature in order to keep the water adsorbed. In other words, the vapour pressure of the water adsorbed on cellulose increases relatively, with rise in temperature, more rapidly than the vapour pressure of free water. These experimental results also show that with rise in temperature the adsorbed water becomes less bound.

A somewhat analogous case was found by Horn and Mennie (5) in the system gelatin-water. Heat capacity measurements on gelatin containing much more water than the cellulose in these experiments seemed to indicate that there was a change in the amount of bound water with the temperature.

Conclusions

A new calorimeter and experimental technique have been devised which are applicable to the measurement of the heat capacities of small amounts of water adsorbed on a colloidal material, with a far greater accuracy than was previously possible. The accuracy could be enhanced by a number of alterations in design and by the use of a platinum thermometer with a Mueller bridge for measuring the temperature. In this way it would be possible to increase the temperature range of the measurements.

The heat capacity of water adsorbed on cellulose up to 12% has been measured for the first time over the temperature range $-35°$ to $+25°C.$, with considerable accuracy, but in order to draw any further conclusions from these measurements it is essential to expand previous investigations into the properties of the cellulose-water system. It is suggested that adsorption isothermals be determined on a sample of the cellulose used over a similar temperature range and also that measurements of the heat of wetting over as large a temperature range as is feasible should be carried out.

Since it is possible that there is a change in the cellulose-water equilibrium with rise in temperature, it may be of practical importance that attention has been drawn to this phenomenon, because all paper processing depends to a large extent on the addition and removal of water. Then, if this hypothesis is substantiated, it may prove to be of value in suggesting alterations in conditions, especially in temperature, under which certain parts of the processing are carried out.

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